

Indoor Air Chemistry: Cleaning Agents, Ozone and Toxic Air Contaminants

Final Report: Contract No. 01-336

Prepared for the California Air Resources Board
and the California Environmental Protection Agency:
California Air Resources Board
Research Division
1001 I Street, 5th Floor
Sacramento, CA 95814

Prepared by:
William W Nazaroff (principal investigator), Beverly K. Coleman, Hugo Destaillats, Alfred T. Hodgson, De-Ling Liu, Melissa M. Lunden, Brett C. Singer, and Charles J. Weschler

Department of Civil and Environmental Engineering
661 Davis Hall
University of California
Berkeley, CA 94720-1710

Indoor Environment Department
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
1 Cyclotron Road
Berkeley, CA 94720

April 2006

Disclaimer

The statements and conclusions in this Report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Acknowledgments

The authors thank Dorothy Shimer, Jeff Yanosky, and Peggy Jenkins of the Research Division of the Air Resources Board for their effective technical management of this project. We acknowledge, with thanks, the experimental contributions of Tosh Hotchi and Michal Landau.

This report was submitted in fulfillment of Contract 01-336, "Indoor air chemistry: Cleaning products, ozone and toxic air contaminants," by the University of California, Berkeley, under the sponsorship of the California Air Resources Board. Work was completed as of 13 May 2006.

Table of Contents

Disclaimer	ii
Acknowledgements.....	iii
Table of Contents.....	iv
List of Figures	vii
List of Tables.....	xi
Abstract	xviii
Executive Summary.....	xix
1. Introduction	1
2. Review: Exposure to Primary and Secondary Air Pollutants Associated with Use of Cleaning Products and Air Fresheners	4
2.1. Introduction.....	4
2.2. Cleaning products and air pollution	4
2.2.1. Emissions and inhalation intake	4
2.2.2. Inhalation pathways	5
2.3. Direct evidence of health hazards	6
2.3.1. Accidental poisonings associated with inappropriate mixing of cleaning agents	6
2.3.2. Asthma, allergy, and respiratory irritation	7
2.4. Composition, primary emissions, and inhalation exposure	7
2.4.1. Emissions.....	8
2.4.2. Dynamic behavior	9
2.4.3. Human factors.....	11
2.5. Reactive chemistry and secondary pollutants	12
2.5.1. Reactions with ozone	12
2.5.2. Reactions with OH and NO ₃	13
2.5.3. Rate comparisons	13
2.5.4. Oxidation products.....	14
2.5.5. Reactions on surfaces.....	16
2.5.6. Influence of reactive chemistry	17
2.6. Conclusion	18
3. Composition and Primary Emissions from Cleaning Products and Air Fresheners.....	35
3.1. Introduction.....	35
3.2. Shelf survey	35
3.2.1. Objectives.....	35
3.2.2. Methods	35
3.2.3. Results	37
3.3. Composition screening experiments	38
3.3.1. Objectives.....	38
3.3.2. Methods	38
3.3.3. Screening results	44
3.3.4. Estimates of potential residential emissions of target VOCs	48
3.4. Emissions and concentrations from simulated-use experiments.....	50
3.4.1. Introduction	50
3.4.2. Methods	51
3.4.3. Results and discussion.....	55

3.5. Study Implications of Evolving California Consumer Product Regulations	59
3.6. Conclusions	60
4. Reactive Chemistry Involving Constituents of Cleaning Products and Air Fresheners	101
4.1. Introduction	101
4.2. Bench-scale chamber experiments: Methods	101
4.2.1. Reaction chamber and ancillary setup	101
4.2.2. Characterization and delivery of household products emissions	102
4.2.3. Sampling and analytical methods	102
4.2.4. Experimental matrix	102
4.2.5. Experimental procedure	103
4.2.6. Determination of OH radical concentration	103
4.2.7. Particle sampling	103
4.2.8. Surface residue experiments	103
4.2.9. Experiments conducted in the presence of NO ₂	104
4.2.10. Data quality and uncertainty	104
4.3. Bench-scale chamber experiments: Results and discussion	104
4.3.1. Reactivity of primary constituents and ozone	104
4.3.2. Volatile oxidation products	106
4.3.3. Determination of hydroxyl radical concentrations	107
4.3.4. Secondary organic aerosol formation	108
4.3.5. Surface application	109
4.3.6. Effect of nitrogen dioxide	110
4.4. Room-scale experiments: Methods	110
4.4.1. Introduction	110
4.4.2. Chamber, products, and application protocols	111
4.4.3. Air quality measurements	112
4.4.4. Data quality and uncertainty	114
4.5. Room-scale experiments: Results and discussion	115
4.5.1. VOC constituents and chamber concentrations	115
4.5.2. Ozone concentrations and reactions	116
4.5.3. OH radical concentrations and reactions	118
4.5.4. Secondary pollutants: Very volatile carbonyls	118
4.5.5. Secondary pollutants: Particle number and mass concentration	119
4.5.6. Relevance to real-world scenarios and exposures	119
4.6. Conclusions	120
5. Implications for Air-Pollutant Exposure	145
5.1. Illustrative exposure scenarios	145
5.1.1. Example 1: Routine cleaning by occupant	145
5.1.2. Example 2: Multi-house cleaning by professional home cleaner	147
5.1.3. Example 3: Cleaning in a small, moderately ventilated bathroom	148
5.1.4. Example 4: Whole-house interior window cleaning	148
5.1.5. Example 5: Air freshener and ozone in a child's bedroom	149
5.1.6. Example 6: Cleaning when outdoor ozone levels are high	150
5.1.7. Example 7: Use of cleaning agents with elevated ozone and NO ₂ levels	150
5.1.8. Summary of the scenario results	151
5.2. Limitations: Chemistry and toxicology	151

5.2.1. Stealth products of ozone-initiated chemistry	151
5.2.2. Lack of toxicological data for oxidation products	152
5.2.3. Knowledge gaps.....	152
5.3. Practical measures to reduce exposures.....	152
6. Summary and Conclusions.....	157
7. Recommendations.....	160
References	162
List of Publications Produced	178
Glossary of Terms, Abbreviations, and Symbols.....	179
Appendix A: Shelf Survey	184
Appendix B: Composition Screening Experiments.....	198
Appendix C: Emissions and Concentrations from Simulated-Use Experiments	206
Appendix D: Reactive Chemistry Bench-Scale Experiments	232
Appendix E: Room-Scale Experiments with Ozone	276

List of Figures

2.1.	Hypothetical concentration of an air contaminant resulting from the primary emissions of a volatile constituent of a cleaning product, used in a single-family home.	33
2.2.	Hypothetical concentrations of air contaminants resulting from the primary emissions of a reactive volatile constituent of a cleaning product, used in a single-family home.	34
3.1.	Chemical structure of terpene hydrocarbons included among target analytes	92
3.2.	Chemical structure of unsaturated, oxygenated compounds included among target analytes.	93
3.3.	Chemical structure of ethylene-based glycol ethers included among target analytes.	94
3.4.	Measured concentrations of 2-butoxyethanol following simulated use of GPC-3 and GPC-4 in selected large chamber experiments.	95
3.5.	Measured concentrations of 2-butoxyethanol following simulated use of GLC-1 (Experiments 1A & 1L) and GPC-2 (Experiment 1M) in large chamber experiments and idealized theoretical time profiles.....	96
3.6.	Measured concentrations of major terpene and terpene-alcohol constituents following application of GPC-1 in large-chamber experiments.....	97
3.7.	Results of experiment 1R, using scented-oil air freshener AFR-1, indicating time-dependent concentrations of selected unsaturated organic compounds, and total rate of air freshener product volatilization.....	98
3.8.	Emitted fraction of 2-butoxyethanol and d-limonene for cleaning-product experiments conducted in 50-m ³ chamber.	99
3.9.	Emitted fraction of terpenes and terpene alcohols associated with use of cleaning product GPC-1.	100
4.1.	Consumption of reactive VOCs from (A) GPC-1, (B) GPD-1, and (C) AFR-1.	135
4.2.	Yield of oxidation products from ozone reaction with volatile components of (A) GPC-1, (B) GPD-1, and (C) AFR-1.....	136
4.3.	Hydroxyl radical concentration versus residual ozone concentration for small-chamber experiments with (A) GPC-1, (B) GPD-1, and (C) AFR-1.....	137
4.4.	SMPS measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with moderate ozone levels (63 ppb in supply air) at 3 ach (Expt 2K).	138
4.5.	SMPS measurements of secondary organic aerosol particles generated when a plate containing dry residue of a pine oil-based cleaner was introduced in the chamber operating at high ozone levels (118 ppb in supply air) at 1 ach (Expt 2L)	139
4.6.	Limonene concentrations in chamber air following application of the orange oil degreaser (GPD-1)	140
4.7.	Constituent concentrations in chamber air following floor mopping with a dilute solution of the pine-oil cleaner (GPC-1)	141
4.8.	Constituent concentrations in chamber air for 1 hour following floor mopping with a dilute solution of the pine oil cleaner (GPC-1)	142
4.9.	Ozone concentration profiles: (a) Exp. 3C: GPD-1 sprayed at $t = 0$; (b) Exp. 3H: mopping with GPC-1 started at $t = 0$; (c) Exp. 3I: mopping with water only; (d)	

Exp. 3K: AFR-1 plugged-in for >24 h then ozone added to chamber air supply starting at $t = 0$.	143
4.10. Particle mass concentrations calculated from the size-resolved particle number concentration data in Exp. 3C, 3G, and 3J.	144
C.1. Cumulative probability distribution for product application rates among 25 subjects instructed to use a trigger-spray product (GPC-3) to clean a 0.93-m ² section of laminate tabletop.	230
C.2. Cumulative probability distribution for product application rate for 11 subjects instructed to use a trigger-spray product (GPC-1) to disinfect a clean 1.16-m ² laminate tabletop.	231
D.1. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with very high ozone levels (253 ppb in supply air) at 3 ach (Expt 2A).	245
D.2. OPC measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with very high ozone levels (253 ppb in supply air) at 3 ach (Expt 2A).	246
D.3. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with high ozone levels (131 ppb in supply air) at 3 ach (Expt 2B).	247
D.4. OPC measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with high ozone levels (131 ppb in supply air) at 3 ach (Expt 2B).	248
D.5. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with high ozone levels (130 ppb in supply air) at 1 ach (Expt 2C).	249
D.6. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with moderate ozone levels (65 ppb in supply air) at 3 ach (Expt 2D).	250
D.7. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with low ozone levels (29 ppb in supply air) at 3 ach (Expt 2E).	251
D.8. OPC measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with low ozone levels (29 ppb in supply air) at 3 ach (Expt 2E).	252
D.9. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPD-1 with high ozone levels (137 ppb in supply air) at 3 ach (Expt 2F).	253
D.10. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPD-1 with high ozone levels (136 ppb in supply air) at 1 ach (Expt 2G).	254
D.11. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPD-1 with moderate ozone levels (63 ppb in supply air) at 3 ach (Expt 2H).	255
D.12. SMPS measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with high ozone levels (126 ppb in supply air) at 3 ach (Expt 2I).	256

D.13. OPC measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with high ozone levels (126 ppb in supply air) at 3 ach (Expt 2I).	257
D.14. SMPS measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with high ozone levels (127 ppb in supply air) at 1 ach (Expt 2J).	258
D.15. OPC measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with high ozone levels (127 ppb in supply air) at 1 ach (Expt 2J).	259
D.16. SMPS measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with moderate ozone levels (63 ppb in supply air) at 3 ach (Expt 2K).	260
D.17. OPC measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with moderate ozone levels (63 ppb in supply air) at 3 ach (Expt 2K).	261
D.18. SMPS measurements of secondary organic aerosol particles generated in the reaction of dried residue of GPC-1 with high ozone levels (118 ppb in supply air) at 1 ach (Expt 2L).	262
D.19. OPC measurements of secondary organic aerosol particles generated in the reaction of dried residue of GPC-1 with high ozone levels (118 ppb in supply air) at 1 ach (Expt 2L).	263
D.20. SMPS measurements of secondary organic aerosol particles generated in the reaction of dried residue of GPD-1 with high ozone levels (114 ppb in supply air) at 1 ach (Expt 2M).	264
D.21. SMPS measurements of secondary organic aerosol particles generated in the reaction of sorbed residue of AFR-1 with high ozone levels (122 ppb in supply air) at 1 ach (Expt 2N).	265
D.22. SMPS measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with high ozone levels (139 ppb in supply air) and NO ₂ levels (75 ppb in supply air) at 3 ach (Expt 2O).	266
D.23. OPC measurements of secondary organic aerosol particles generated in the reaction of GPC-1 with high ozone levels (139 ppb in supply air) and NO ₂ levels (75 ppb in supply air) at 3 ach (Expt 2O).	267
D.24. Response of ozone analyzer in Expt 2A.	268
D.25. Response of ozone analyzer in Expt 2B.	268
D.26. Response of ozone analyzer in Expt 2C.	269
D.27. Response of ozone analyzer in Expt 2D.	269
D.28. Response of ozone analyzer in Expt 2E.	270
D.29. Response of ozone analyzer in Expt 2F.	270
D.30. Response of ozone analyzer in Expt 2G.	271
D.31. Response of ozone analyzer in Expt 2H.	271
D.32. Response of ozone analyzer in Expt 2I.	272
D.33. Response of ozone analyzer in Expt 2J.	272
D.34. Response of ozone analyzer in Expt 2K.	273
D.35. Response of ozone analyzer in Expt 2L.	273
D.36. Response of ozone analyzer in Expt 2M.	274

D.37.	Response of ozone analyzer in Expt 2N.....	274
D.38.	Time-dependent concentrations of ozone, NO ₂ , and NO in Expt 2O	275
E.1.	OPC measurements of aerosol particles during Expt 3A (GPD-1, no ozone).....	307
E.2.	OPC measurements of aerosol particles during Expt 3B (GPD-1, no ozone).....	308
E.3.	OPC measurements of aerosol particles during Expt 3C (GPD-1, with ozone).....	309
E.4.	OPC measurements of aerosol particles during Expt 3D (GPC-1, no ozone).....	310
E.5.	OPC measurements of aerosol particles during Expt 3E (GPC-1, no ozone).	311
E.6.	OPC measurements of aerosol particles during Expt 3F (GPC-1, with ozone).....	312
E.7.	OPC measurements of aerosol particles during Expt 3G (GPC-1, with ozone).....	313
E.8.	OPC measurements of aerosol particles during Expt 3H (GPC-1, with ozone).....	314
E.9.	OPC measurements of aerosol particles during Expt 3I (water mopping, with ozone).	315
E.10.	OPC measurements of aerosol particles during Expt 3J (AFR-1 at setting 1).	316
E.11.	OPC measurements of aerosol particles during Expt 3K (AFR-1 at setting 3).	317
E.12.	Response of ozone analyzer in experiment 3A (no ozone in supply air).....	318
E.13.	Response of ozone analyzer in experiment 3B (no ozone in supply air)	318
E.14.	Response of ozone analyzer in experiment 3C (ozone in supply air)	319
E.15.	Response of ozone analyzer in experiment 3D (ozone in supply air).....	319
E.16.	Response of ozone analyzer in experiment 3E (no ozone in supply air)	320
E.17.	Response of ozone analyzer in experiment 3F (ozone in supply air)	320
E.18.	Response of ozone analyzer in experiment 3G (ozone in supply air).....	321
E.19.	Response of ozone analyzer in experiment 3H (ozone in supply air).....	321
E.20.	Response of ozone analyzer in experiment 3I (ozone in supply air)	322
E.21.	Response of ozone analyzer in experiment 3J (ozone in supply air starting at $t = 0$)....	322
E.22.	Response of ozone analyzer in experiment 3K (ozone in supply air starting at $t =$ 0)	323
E.23.	Chamber air temperature versus time in experiments 3A, 3B, and 3C.....	324
E.24.	Chamber air temperature versus time in experiments 3D, 3E, 3F, 3G, and 3H	325
E.25.	Chamber air temperature versus time in experiments 3J and 3K	326
E.26.	Chamber relative humidity versus time in experiments 3A, 3B, and 3C.....	327
E.27.	Chamber relative humidity versus time in experiments 3D, 3E, 3F, 3G, and 3H	328
E.28.	Chamber relative humidity versus time in experiments 3J and 3K	329

List of Tables

ES-1. Peak one-hour-average air concentrations of selected chemicals from simulated cleaning product use.....	xxii
ES-2. Reactive chemistry observed in bench-scale (198 liter) chamber when volatile components of pine-oil based cleaning product GPC-1 were combined with ozone	xxiii
ES-3. Concentrations of secondary pollutants from simulated use of cleaning products and air freshener in the presence of ozone	xxiv
2.1. Estimated atmospheric emissions of volatile organic compounds from use of household and commercial cleaning products and air fresheners in California, 1997.....	19
2.2. Mechanisms by which use of cleaning products can influence inhalation exposure to air pollutants.	20
2.3. Documented inhalation toxicity related to mixing of cleaning products.	21
2.4. Documented associations of asthma, allergy, and sick-building syndrome symptoms in relation to cleaning product use	22
2.5a. Reported volatile constituents of cleaning products listed under California's Proposition 65 or as a Toxic Air Contaminant	23
2.5b. Compounds included in a California emissions inventory of reactive organics for household products that are also listed in the California Toxic Air Contaminant identification program	25
2.6. Sorption studies of target cleaning-product chemicals on indoor surface materials	27
2.7. Constituents of cleaning product and air fresheners containing C=C bonds.....	28
2.8. Reported 2 nd order rate constants, <i>k</i> , and calculated pseudo 1 st order rate constants, <i>k'</i> , for the reactions of selected unsaturated constituents of cleaning products and air fresheners with ozone, hydroxyl radicals and nitrate radicals.....	30
2.9. Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals.	31
2.10. Summary of findings from literature review	32
3.1. Number of retail outlets in California's 15 largest cities for ten major corporations selling consumer products.	61
3.2. Locations of five surveyed retail stores.....	62
3.3. ARB consumer product categories surveyed.....	62
3.4. Number of consumer products and represented manufacturers by category at each store surveyed.	63
3.5. Number of consumer products by category for 18 manufacturers with three or more products in shelf survey.....	64
3.6. Summary information for 50 products selected from shelf survey as potential candidates for further study.	65
3.7. Consumer products investigated in experiments performed during this research	66
3.8. Target compounds.....	67
3.9. Mass fractions of ozone-reactive VOCs in three containers (A, B and C) of general purpose cleaner GPC-1 determined by bag method	68
3.10. Mass fractions of ethylene-based glycol ethers in three containers (A, B and C) of glass cleaner GLC-1 determined by bag method.....	68

3.11.	Mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers determined by bag method analysis of four cleaning products with >3% d-limonene	69
3.12.	Mass fractions of ozone-reactive VOCs determined by bag method analysis of three cleaning products with pine oil constituents	70
3.13.	Mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers determined by bag method analysis of six cleaning products with >0.5% 2-butoxyethanol	71
3.14.	Mass fractions of ozone-reactive VOCs determined by bag method analysis of five cleaning products with <0.2% of individual target compounds	72
3.15.	Mass fractions of ozone-reactive VOCs determined by bag method analysis of four air-freshener products	73
3.16.	Mass fractions of d-limonene and total ozone-reactive VOCs determined by bag method analysis of consumer products	74
3.17.	Additional abundant compounds detected by bag method analysis of consumer products	75
3.18.	Comparison of product mass fraction formulations of d-limonene and 2-butoxyethanol as reported by manufacturers in Material Safety Data Sheets with mass fractions determined by bag method analysis of six cleaning products	76
3.19.	Comparison of mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers in general-purpose cleaners GPC-1 and GPC-4 determined by direct analysis of products diluted in methanol and by bag method analysis of vapor-phase.....	77
3.20.	Comparison of mass fractions of ethylene-based glycol ethers in cleaning products DIS-1, GPC-3, and GLC-1 determined by direct analysis of products diluted in methanol and by bag method analysis of vapor-phase	78
3.21.	Applications considered for a disinfectant and other cleaning products.....	79
3.22.	Dilution factors interpreted from information on manufacturers' product labels for various cleaning applications of a disinfectant and five general-purpose cleaners	80
3.23.	Cleaning tasks and cleaning surface areas estimated to be typical for a 140-m ² three-bedroom, two-bath house	81
3.24.	Estimated consumer product use rates (g/use) and potential emissions (g/use) of ozone-reactive VOCs and ethylene-based glycol ethers for cleaning products and plug-in air fresheners.....	82
3.25.	Summary information for six products employed in simulated-use experiments.	83
3.26.	Summary of 18 simulated-use experiments conducted in 50-m ³ chamber	84
3.27.	Concentration (g L ⁻¹) of d-limonene and ethylene-based glycol ethers in five cleaning products determined by direct analysis of product diluted in methanol	84
3.28.	Composition of GPC-1 determined by direct analysis of product diluted in methanol.	85
3.29.	Composition, chamber air concentrations, and emission factors for terpenoids and other VOCs in scented-oil air freshener, AFR-1.	86
3.30.	Emission factors and initial chamber air concentrations for d-limonene and ethylene-based glycol ethers associated with simulated cleaning activities.	87
3.31.	Emission factors and initial chamber air concentrations of terpenes and terpene alcohols associated with use of GPC-1.	88

3.32.	Summary of key California consumer product regulations concerning the reactive volatile organic compound content of cleaning product classes included in the present study.	89
3.33.	Summary of findings from composition characterization and primary emissions experiments.....	90
4.1.	Summary of experimental conditions for investigating reactive chemistry between ozone and two cleaning products (GPC-1 and GPD-1) and one air freshener (AFR-1) in a bench-scale chamber	122
4.2.	Reaction of ozone with components of pine oil-based cleaner (GPC-1) in bench-scale chamber experiments.....	123
4.3.	Reaction of ozone with d-limonene from orange oil-based degreaser (GPD-1) in bench-scale chamber experiments.	124
4.4.	Reaction of ozone with air freshener components (AFR-1) in bench-scale experiments.....	125
4.5.	Reaction of ozone with components of pine oil-based cleaner (GPC-1) in bench-scale chamber experiments, with and without the presence of NO ₂	126
4.6.	Data summary for secondary organic aerosol formation in bench-scale chamber experiments with two cleaning products (GPC-1 and GPD-1) and one air freshener (AFR-1)	127
4.7.	Summary of experiments involving simulated use of cleaning products (GPD-1 and GPC-1) and an air freshener (AFR-1), investigating the influence of ozone	128
4.8.	Time-averaged concentrations (ppb) of GPC-1 constituents during experiments 3D-3H.....	129
4.9.	Chamber air concentrations and percent reacted of AFR-1 constituent terpenoids and other VOCs based on concentrations measured 0-5 h before and 3-5 h after ozone was introduced into the supply air at 114 ppb (Expt 3J).....	130
4.10.	Measured TMB/PCE ratios and calculated OH concentrations for selected experiments.....	131
4.11.	Measured concentrations (ppb) of very volatile carbonyls	131
4.12.	Secondary fine particulate matter formed during use of consumer products in relation to the presence of ozone	132
4.13.	Summary of findings from reactive chemistry experiments	133
5.1.	Estimated annual inhalation intake of 2-butoxyethanol (2-BE), formaldehyde (HCHO), and secondary organic aerosol (SOA) for occupant of home or large apartment who does her/his own cleaning.....	154
5.2.	Annual estimated inhalation intake of 2-butoxyethanol (2-BE), formaldehyde (HCHO), and secondary organic aerosol (SOA) for person employed as a domestic cleaner.....	155
5.3.	Key findings from illustrative exposure scenarios related to cleaning product and air freshener use	156
A.1.	Results of consumer product shelf survey for disinfectants.....	185
A.2.	Results of consumer product shelf survey for general-purpose degreasers and multipurpose solvents.....	186
A.3.	Results of consumer product shelf survey for general-purpose cleaners.	187
A.4.	Results of consumer product shelf survey for glass cleaners.	190

A.5.	Results of consumer product shelf survey for dusting aids, furniture maintenance products, and wood cleaners.....	191
A.6.	Results of consumer product shelf survey for carpet and upholstery cleaners and spot removers.....	192
A.7.	Results of consumer product shelf survey for floor polishes or waxes and floor wax strippers.....	193
A.8.	Results of consumer product shelf survey for specialty cleaners including bathroom and tile cleaners, metal polish/cleaners, and oven cleaners.	194
A.9.	Results of consumer product shelf survey for air fresheners.....	195
B.1.	Mass fractions of target VOCs determined by bag method analysis of individual samples of four products with >3% d-limonene.....	199
B.2.	Mass fractions of target VOCs determined by bag method analysis of individual samples of three products with pine oil constituents	200
B.3.	Mass fractions of target VOCs determined by bag method analysis of individual samples of two products with >2% 2-butoxyethanol.....	201
B.4.	Mass fractions of target VOCs determined by bag method analysis of individual samples of three products with >1% 2-butoxyethanol.....	202
B.5.	Mass fractions of target VOCs determined by bag method analysis of individual samples of glass cleaner GLC-1.	203
B.6.	Mass fractions of target VOCs determined by bag method analysis of individual samples of products with <0.2% of target analytes.	204
B.7.	Mass fractions of target VOCs determined by bag method analysis of individual samples of air fresheners.	205
C.1.	Product containers used for solvent dilution, bag screening and large chamber emissions experiments.....	208
C.2.	Product containers used for each experimental approach.	209
C.3.	Samples analyzed in solvent dilution determination of GLC-1 composition.....	210
C.4.	Samples analyzed in solvent dilution determination of GPC-2 composition.....	210
C.5.	Samples analyzed in solvent dilution determination of GPC-3 composition.....	210
C.6.	Samples analyzed in solvent dilution determination of GPC-4 composition.....	210
C.7.	Quantified constituents of GPC-1.....	211
C.8.	Samples analyzed in solvent dilution determination of GPC-1 composition.....	212
C.9.	Samples analyzed in solvent dilution determination of AFR-1 composition (Bottle B).....	213
C.10.	Results of product application rate survey, with cleaner GPC-3 in trigger spray bottle.....	214
C.11.	Results of product application rate survey for disinfection.....	215
C.12.	Measured masses (g) of solutions and cleaning equipment during mopping experiments.....	216
C.13.	Measured masses (grams) of cleaning products and equipment for full strength, counter cleaning experiments	217
C.14.	Airborne concentrations of glycol ethers for experiment 1A (GLC-1, counter).	218
C.15.	Airborne constituent concentrations ($\mu\text{g m}^{-3}$) for experiment 1B (GPC-1, counter).....	218
C.16.	Airborne concentrations of 2-butoxyethanol for experiment 1C (GPC-3, counter).	219
C.17.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1D (GPC-4, counter).....	219

C.18.	Airborne constituent concentrations ($\mu\text{g m}^{-3}$) for experiment 1E (GPC-1, counter)	220
C.19.	Airborne concentrations of 2-butoxyethanol for experiment 1F (GPC-3, counter).....	222
C.20.	Airborne concentrations of 2-butoxyethanol for experiment 1G (GPC-3, counter).....	222
C.21.	Airborne concentrations of 2-butoxyethanol for experiment 1H (GPC-3, counter).....	223
C.22.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1I (GPC-4, counter).....	223
C.23.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1J (GPC-4, counter).....	223
C.24.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1K (GPC-4, counter).....	224
C.25.	Airborne concentrations of glycol ethers for experiment 1L (GLC-1, counter).....	224
C.26.	Airborne concentrations of 2-butoxyethanol for experiment 1M (GPC-2, counter).	225
C.27.	Airborne constituent concentrations ($\mu\text{g m}^{-3}$) for experiment 1N (GPC-1, mopping).....	225
C.28.	Airborne concentrations of 2-butoxyethanol for experiment 1O (GPC-3, mopping).....	227
C.29.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1N (GPC-1, mopping).....	227
C.30.	Airborne concentrations of 2-butoxyethanol and d-limonene for experiment 1O (GPC-3, mopping).....	228
C.31.	Airborne constituent concentrations ($\mu\text{g m}^{-3}$) for experiment 1R (AFR-1).	229
D.1.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2A (GPC-1).	233
D.2.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2A (GPC-1).	233
D.3.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2B-I (GPC-1)	233
D.4.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2B-I (GPC-1)	234
D.5.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2B-II (GPC-1)	234
D.6.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2B- II (GPC-1).....	234
D.7.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2B- III (GPC-1)	235
D.8.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2B- III (GPC-1)	235
D.9.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2C (GPC-1)	236
D.10.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2C (GPC-1)	236
D.11.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2D (GPC-1)	236
D.12.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2D (GPC-1)	237

D.13.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2E (GPC-1)	237
D.14.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2E (GPC-1)	237
D.15.	Airborne d-limonene concentrations (mg m^{-3}) measured in experiment 2F (GPD-1)	238
D.16.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2F (GPD-1)	238
D.17.	Airborne d-limonene concentrations (mg m^{-3}) measured in experiment 2G (GPD-1)	238
D.18.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2G (GPD-1)	239
D.19.	Airborne d-limonene concentrations (mg m^{-3}) measured in experiment 2H (GPD-1)	239
D.20.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2H (GPD-1)	239
D.21.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2I (AFR-1)	240
D.22.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2I (AFR-1)	240
D.23.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2J (AFR-1)	240
D.24.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2J (AFR-1)	241
D.25.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2K (AFR-1)	241
D.26.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2K (AFR-1)	241
D.27.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2L (GPC-1)	242
D.28.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2L (GPC-1)	242
D.29.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2N (GPD-1)	242
D.30.	Airborne concentrations of primary VOCs (mg m^{-3}) measured in experiment 2O (GPC-1)	243
D.31.	Airborne oxidation product concentrations (mg m^{-3}) measured in experiment 2O (GPC-1)	243
D.32.	Summary of ozone concentration data from experiments in bench-scale chamber.....	244
E.1.	Airborne concentrations of d-limonene measured in experiment 3B (GPD-1).....	279
E.2.	Airborne concentrations of d-limonene measured in experiment 3C (GPD-1).....	280
E.3.	Airborne time-integrated concentrations of primary VOCs (ppb) in experiment 3D (GPC-1)	281
E.4.	Airborne, time-resolved concentration measurements of primary VOCs (ppb) in experiment 3E (GPC-1).....	283

E.5.	Airborne time-integrated concentrations of primary VOCs (ppb) in experiment 3E (GPC-1)	286
E.6.	Airborne, time-resolved concentration measurements of primary VOCs (ppb) in experiment 3F (GPC-1)	287
E.7.	Airborne time-integrated concentrations of primary VOCs (ppb) in experiment 3E (GPC-1)	289
E.8.	Airborne, time-resolved concentration measurements of primary VOCs (ppb) in experiment 3G (GPC-1)	291
E.9.	Airborne, time-integrated concentrations of primary VOCs (ppb) in experiment 3G (GPC-1)	294
E.10.	Airborne, time-resolved concentration measurements of primary VOCs (ppb) in experiment 3H (GPC-1)	295
E.11.	Airborne, time-integrated concentrations of primary VOCs (ppb) in experiment 3H (GPC-1)	298
E.12.	Airborne concentration measurements of primary VOCs (ppb) in experiment 3J (AFR-1)	299
E.13.	Airborne concentrations measurements of primary VOCs (ppb) in experiment 3K (AFR-1)	300
E.14.	Sample information and results for PCE and TMB, Expt 3C	301
E.15.	Sample information and results for PCE and TMB, Expt 3E.....	302
E.16.	Sample information and results for PCE and TMB, Expt 3G	302
E.17.	Sample information and results for PCE and TMB, Expt 3H	303
E.18.	Sample information and results for PCE and TMB, Expt 3I.....	303
E.19.	Sample information and results for PCE and TMB, Expt 3J.....	304
E.20.	Sample information and results for PCE and TMB, Expt 3K	304
E.21.	Airborne concentrations of very volatile carbonyls (ppb), measured in experiments 3A-3K	305

Abstract

When cleaning products and air fresheners are used indoors, occupants are exposed to airborne chemicals, potentially leading to health risks. Indoor air pollutant exposures owing to cleaning product and air freshener use depend on emissions from products, dynamic behavior of chemical species, and human factors. A series of experiments was conducted to investigate volatile organic compound emissions, concentrations, and reactive chemistry associated with the household use of cleaning products and air fresheners. Research focused on two common classes of ingredients in cleaning products and air fresheners: ethylene-based glycol ethers, which are classified as toxic air contaminants, and terpenes, which react rapidly with ozone. A shelf-survey of retail outlets led to the selection of 21 products whose chemical composition was characterized. Among the criteria used to select these products were ready availability through California retail outlets and, for the majority of products, expectation that they contained ethylene-based glycol ethers, terpenes and related compounds, or both. Of the 17 cleaning products characterized, four contained substantial levels of d-limonene (4-25% by mass), three contained terpenoids that are characteristic of pine oil, six contained substantial levels of ethylene-based glycol ethers (0.8-10% by mass), and five contained less than 0.2% of any of the target analytes. Xylene in one product was the only other toxic air contaminant detected. Among the four air fresheners characterized, three contained substantial quantities (9-14% by mass) of terpene hydrocarbon and terpene alcohol constituents, with linalool being the most abundant. Six of the 21 products were investigated in simulated-use experiments in which emissions and concentrations of primary constituents were measured. Cleaning products that contain 2-butoxyethanol as an active ingredient produced one-hour-average concentrations of 300 to 2,300 $\mu\text{g}/\text{m}^3$ immediately after simulated typical use in a room-sized chamber. For cleaning products that contain d-limonene as an active ingredient, corresponding levels were 1,000 to 6,000 $\mu\text{g}/\text{m}^3$. Application of a pine-oil based cleaner produced one-hour-average concentrations of 10-1300 $\mu\text{g}/\text{m}^3$ for terpene hydrocarbons and terpene alcohols. Reactive chemistry was studied by exposing constituents of three products to ozone, both in a bench-scale chamber and during simulated use. Prominent products of the reaction of terpenes with ozone included formaldehyde (a toxic air contaminant), hydroxyl radical, and secondary organic aerosol (a form of fine particulate matter). Incorporating the new experimental data, exposures were estimated for several simulated use scenarios. Under ordinary circumstances, exposures to 2-butoxyethanol, formaldehyde, and secondary organic aerosol are not expected to be as high as guideline values solely as a result of cleaning product or air freshener use. However, ordinary use could lead to exposure levels of similar magnitude as guideline values. Scenario model results suggest that exposure levels could exceed guideline values under exceptional yet plausible conditions, such as cleaning a large surface area in a small room. The results of this study provide important information for understanding the inhalation exposures to certain air pollutants that can result from the use of common household products.

Executive Summary

Background

Exposures to air pollutants cause health risks. The strategic plan of the California Air Resources Board (ARB) recognizes the importance of developing better knowledge of human exposure to air pollutants (<http://www.arb.ca.gov/research/apr/apr.htm>). The volatile organic compound (VOC) composition of consumer products sold in California is regulated by ARB to limit their contribution to photochemical smog production (<http://www.arb.ca.gov/consprod/consprod.htm>). However, use of cleaning products and air fresheners in indoor environments can also lead to the direct exposure of product users and other building occupants to air pollutants. Exposures of potential concern can occur because certain consumer products may be formulated with VOCs that are classified as toxic air contaminants (TACs). Of interest in this category are ethylene-based glycol ethers, which are classified as TACs, although with relatively low toxicities. These compounds are commonly used as solvents in cleaning products, causing many people to be routinely exposed as the products are used during household cleaning activities. Additional exposures of potential concern arise owing to reactive chemistry that occurs in the indoor environment. This chemistry converts nontoxic primary constituents into secondary pollutants that may pose human health risks. Of particular interest in this category are terpene-ozone reactions. Terpenes, a class of VOCs derived from plant oils, are widely used in cleaning products and air fresheners because of their favorable solvent properties and pleasant odors. Ozone generated in outdoor air enters indoor environments along with ventilation air. Ozone may also be emitted directly indoors from certain types of air cleaners and from photocopiers and printers. Some terpenes and related organic compounds react rapidly with ozone. Ozone-terpene chemistry produces the hydroxyl radical, which triggers an array of indoor chemical reactions, and formaldehyde, a TAC with a low acceptable exposure limit. This chemistry also converts some of the gaseous species into organic particulate matter, raising possible concerns because of the strong association between ambient particulate matter levels and a host of adverse health effects. The main objective of this research was to substantially increase our knowledge of the concentrations of air pollutants, especially TACs that occur in indoor environments owing to the use of widely available cleaning products and air fresheners, with and without the simultaneous presence of ozone.

Methods

The broad objective stated in the previous paragraph was achieved by the following means. First, we undertook a thorough review of published literature on air pollutant exposure associated with the use of cleaning products and air fresheners. Next, we conducted a shelf-survey of products that were available to consumers at five retail outlets in northern California. In a multistage process, 21 products were selected for further study considering these key criteria: (a) products are readily available to California consumers through retail outlets; (b) most products are either known or expected to contain substantial levels of reactive terpenes, terpene alcohols, other unsaturated compounds, or ethylene-based glycol ethers; and (c) the set of products includes at least one each of disinfectants, general-purpose degreasers, general-purpose cleaners, wood cleaners, furniture maintenance products, spot removers, multi-purpose solvents, and air fresheners. Then, we conducted measurements to characterize the VOC composition of the selected cleaning products and air fresheners. Using these results, six products were selected to study emissions and concentrations of the primary constituents during eighteen simulated-use experiments in a room-size research chamber. Three products were selected from the set of 21 to

study secondary pollutant formation when combined with ozone. Fifteen experiments were carried out in a bench-scale chamber under well-controlled conditions. With the same products, eleven experiments were executed employing simulated use in the room-sized chamber, with and without the presence of ozone. These experiments examined the effect of ozone on the primary VOC constituents of the cleaning products and air freshener, as well as the resultant production of secondary pollutants, including formaldehyde, the hydroxyl radical, and fine particulate matter. Finally, analyses were carried out to interpret the new experimental results to better understand their significance for human inhalation exposure to air pollutants owing to the use of cleaning products and air fresheners indoors.

Results

Among the 21 products whose composition was tested, six contained ethylene-based glycol ethers, primarily 2-butoxyethanol, with levels ranging from 0.8% to 9.6%. Only one other toxic air contaminant, xylene, was detected, and in only one product. Twelve of the 21 products contained terpenes and other ozone-reactive compounds at overall levels ranging from 0.2% to 26%. Simulated full-strength use of cleaning products caused fractional emissions of terpenes and glycol ethers of 35-100% of the amount dispensed when towels were retained in the test chamber versus 20-50% when towels were removed. Floor mopping with a dilute solution of pine-oil based cleaner led to terpene emissions of 7-12% of the amount dispensed. Simulated cleaning product use caused peak 1-h average concentrations of the most prevalent target compounds to be in the range of a few hundred to a few thousand micrograms per cubic meter, as illustrated in Table ES-1.

When terpenes and related compounds in cleaning products and air fresheners were exposed to ozone, we consistently observed a high degree of reactive chemistry. The effects included reduced concentrations of primary constituents of the products, reduced ozone concentrations, enhanced concentrations of formaldehyde, measurable levels of the OH radical, and substantial secondary production of particulate matter. Table ES-2 illustrates this point by presenting data on ozone and volatile organic compounds from one experiment in which volatile constituents of a pine-oil-based cleaner were exposed to ozone.

Each of the fifteen experiments conducted in the bench-scale chamber produced a nucleation event in which substantial amounts of new ultrafine particles were generated as a consequence of the reactive chemistry. In the eleven room-scale simulated use experiments, we also observed substantial secondary pollutant formation, as illustrated in Table ES-3. The use of a terpene-containing cleaning product or air freshener in the presence of ozone (delivered through the ventilation supply air at 114-120 ppb) increased the formaldehyde levels by 6-12 ppb. The significance of regularly repeated exposures at such levels might be considered against California's chronic reference exposure level for formaldehyde of 2 ppb. Likewise, the use of a terpene-containing cleaning product in the presence of ozone increased the fine particulate matter concentrations by approximately 30-90 micrograms per cubic meter. California's standard for ambient fine particulate matter (PM_{2.5}) is 12 micrograms per cubic meter on an annual average basis. California also has a 24-hour average standard of 50 micrograms per cubic meter for ambient levels of all particulate matter smaller than 10 micrometers in diameter.

Conclusions

The study results indicate that, in California and elsewhere, elevated inhalation exposures to air pollutants can be expected to occur under some circumstances owing to the use of common cleaning products and air fresheners. Several of the products studied contained and emitted substantial amounts of a single TAC, 2-butoxyethanol. This ethylene-based glycol ether was found to be an active ingredient in six of the 21 products characterized. The measured peak concentrations of 2-butoxyethanol owing to the use of these products were below relevant acute exposure guidelines. However, modeled exposures for high-use scenarios suggest that the California acute (one-hour) exposure level of 14 mg m^{-3} might be exceeded under some circumstances. Also of potential concern are the terpenes and related unsaturated organic compounds. These constituents are widely used as solvents and as scenting agents. Many species in this class react rapidly with ozone, leading to the formation of formaldehyde, a TAC with a low chronic reference exposure level, and particulate matter, a regulated pollutant class in ambient air. Other oxidation products are also formed with unknown toxicological properties (e.g., hydroperoxides from linalool.) Thus, it appears that, when compared with health-based concentration guidelines and standards, the levels of 2-butoxyethanol, formaldehyde and particulate matter associated with the use of certain consumer products can be high enough under some circumstances to warrant further consideration. Further consideration should also be given to the toxicological properties of yet-to-be-evaluated oxidation byproducts of ozone-terpene chemistry.

Table ES-1. Peak one-hour-average air concentrations of selected chemicals from simulated cleaning-product use (§3.4). ^a

Experiment ^b	Species concentration (micrograms per cubic meter)			
	2-Butoxyethanol	d-Limonene	Terpinolene	α-Terpineol
Counter cleaning with glass cleaner GLC-1, full strength (1A, 1L)	270, 330			
Counter cleaning with general-purpose cleaner GPC-1, full strength (1B, 1E)		960, 1100	890, 1040	260, 340
Counter cleaning with general-purpose cleaner GPC-3, full strength (1C, 1F-1H)	1540-2300			
Counter cleaning with general-purpose cleaner GPC-4, full strength (1D, 1I-1K)	2170-2530	640-730		
Floor mopping with general-purpose cleaner GPC-1, dilute (1N)		1130	1270	700
Floor mopping with general-purpose cleaner GPC-3, dilute (1O)	1300			
Floor mopping with general-purpose cleaner GPC-4, dilute (1P, 1Q)	380, 1150	2900, 6200		

^a Experiments conducted in 50 cubic meter (1800 cubic foot) chamber ventilated at approximately one air change every two hours. For counter cleaning, area cleaned was 0.56 square meters (6 square feet). Floor mopping was applied to an area of 3.9 square meters (42 square feet). Product usage was designed to be in the upper part of the normal range for residential use. Concentrations reflect the time-average value for chamber air during the first hour following the start of cleaning activity.

^b Experiment number noted in parentheses.

Table ES-2. Reactive chemistry observed in bench-scale (198 liter) chamber when volatile components of pine-oil based cleaning product GPC-1 were combined with ozone (§4.2-4.3). ^a

Species	Concentration (ppb) ^b	Reacted (%) ^c	Yield (%) ^d
Ozone	130	94	
<i>Selected VOC components of cleaning product</i>			
α -Terpinene	25	89	
d-Limonene	229	15	
Terpinolene	266	33	
γ -Terpineol	12	19	
<i>Volatile oxidation products</i>			
Formaldehyde	35		27
Acetaldehyde	2		1
Acetone	83		63
Glycolaldehyde	12		5
Formic acid	12		9
Acetic acid	22		17

^a Results presented for Experiment 2C. Air-exchange rate was 1.0 chamber volumes per hour.

^b For ozone and “selected VOC components of cleaning product,” concentrations are the levels in the chamber air in the absence of reactive chemistry. For “volatile oxidation products,” concentrations are the steady-state levels in the chamber air owing to reactive chemistry between ozone and the primary cleaning product constituents.

^c Reacted (%) represents the proportional reduction of the constituent concentration in chamber air owing to reactive chemistry.

^d Yield (%) represents the moles of product formed per mole of ozone consumed owing to reactive chemistry.

Table ES-3. Concentrations of secondary pollutants from simulated use of cleaning products and air freshener in the presence of ozone (§4.4-4.5). ^a

Experiment ^b	HCHO (ppb) ^c		PM_{1.1} (µg m⁻³) ^c	
	No ozone	Ozone ^d	No ozone	Ozone ^d
Surface cleaning with general-purpose degreaser GPD-1, full strength (3A-3C)	8	20	2	89
Floor mopping with general-purpose cleaner GPC-1, dilute (3D-3H)	7	13	3	34
Air freshener, scented-oil plug-in, AFR-1 (3J-3K)	5	11	1	4

^a Experiments conducted in 50 cubic meter (1800 cubic foot) chamber ventilated at approximately one air change every hour. For surface cleaning, amount of product dispensed was 3.7 g to clean an area of 0.11 square meters (1 square foot). For floor mopping, approximately 50 g of product was used in a dilute aqueous solution to mop an area of 3.9 square meters (42 square feet). The air freshener was plugged into an electrical outlet.

^b Experiment number noted in parentheses.

^c HCHO is formaldehyde. PM_{1.1} represents the fine particle mass concentration. For the cleaning products, values represent 12-hour averages commencing with the start of the cleaning activity. For the air freshener, HCHO concentrations reflect three-hour averages immediately before, or beginning two hours after the onset of ozone supply. PM_{1.1} concentrations reflect 5-hour averages immediately before and immediately after the onset of ozone supply.

^d Ozone was provided in the supply air at a level of 114-120 ppb; residual chamber concentration was approximately 60 ppb absent cleaning product or air freshener, but was as low as 5 ppb during the first hour after the cleaning activity.

1. INTRODUCTION

The use of certain common cleaning products and air fresheners indoors can cause an increase in the indoor airborne concentrations of gaseous and particulate species. When these increases occur in occupied spaces, human inhalation exposures to the species will result. In the event that harmful species are directly released from a product, there may be increases in adverse health risks. Because of the large fraction of time people spend indoors, such increases are of potential concern.

In addition to direct emissions, secondary pollutant formation is of concern. In particular, there is evidence suggesting that ozone-terpene reactions may be of considerable importance indoors. Such reactions can generate toxic air contaminants (TACs), such as formaldehyde. These reactions also produce hydroxyl radicals, which can react with many species, altering TAC levels.

Ozone mainly enters buildings from outdoors as a pollutant in the ventilation air. Indoor sources also exist, including photocopiers, electrostatic air filters and ozone generators. In the absence of indoor sources, concentrations indoors are lower than outdoors because ozone reacts with indoor surfaces and certain gaseous contaminants. Typical indoor-outdoor ozone ratios are 0.2-0.7 (Weschler, 2000), so peak indoor levels in the range of 30-100 ppb are expected when ambient pollution levels are high. Terpenes, such as *d*-limonene and α -pinene, are volatile organic compound (VOC) constituents of products that are used indoors. For example, terpenes are widely used as scenting agents in cleaning products (Weschler and Shields, 1996; Wolkoff et al., 1998; Zhu et al., 2001). Indoor terpene levels of several ppb are common and concentrations in excess of 100 ppb have been reported (Weschler, 2000). One may also infer that elevated concentrations occur by the following logic. The odor thresholds of limonene and pinene are 440 ppb and 700 ppb, respectively (Devos et al., 1990; Mølhave et al., 2000). Because the odor of terpenes is commonly detected when certain cleaning agents are used, short-term peak concentrations of terpenes in indoor air may approach or exceed ppm levels.

Ozone reacts rapidly with terpenes. For example, the lifetimes of *d*-limonene and α -pinene in the presence of 50 ppb ozone are 0.75 and 1.8 h, respectively (Weschler, 2000). The residence time of air indoors before being replaced by ventilation is typically a few hours. Thus, the reactions are fast enough for significant secondary-product formation to occur before reactants are removed by air exchange.

The direct products of ozone-terpene reactions include formaldehyde (Hatakeyama et al., 1989). Existing information at the time this project was started indicated that formation of formaldehyde by ozone-terpene chemistry indoors is potentially significant, capable of contributing tens of ppb to indoor levels on a transient basis.

Another product of ozone-terpene chemistry is the hydroxyl radical (OH). The OH yield for ozone-terpene reactions is high: 0.85 for α -pinene and 0.86 for *d*-limonene, for example (Weschler and Shields, 1996). This is important, because OH reacts rapidly with a broad spectrum of VOCs and its presence in indoor air may, therefore, influence pollutant concentrations. Under simulated but realistic conditions in an office, Weschler and Shields (1997a) used an indirect measurement technique to estimate that OH levels were $\sim 7 \times 10^5$ molecules cm^{-3} when ozone and *d*-limonene were simultaneously elevated to ~ 100 ppb each. Although less than the midday peak for polluted conditions (5×10^6 molecules cm^{-3}), this OH level is sufficiently high to affect indoor concentrations of certain TACs.

A third potentially important product of ozone-terpene chemistry is secondary organic aerosol (Weschler and Shields, 1999; Long et al., 2000; Wainman et al., 2000). When ozone

reacts with terpenes, the products formed include oxygenated organic compounds with higher molecular weight, increased polarity, and reduced vapor pressure relative to the parent compounds. These products, which include organic acids and aldehydes, can condense from the gas phase, adding to airborne particulate matter. Under some circumstances, the condensation will occur on preexisting particles, causing their size and mass to increase. If the rate of formation of these secondary products is sufficiently fast, new ultrafine particles may be formed through a nucleation process. Any mechanism leading to significant particle generation in air that humans breathe raises concern about the potential for associated health risks.

In summary, VOC constituents of cleaning products and air fresheners are common components of indoor air. There are at least three pathways by which the use of these products may affect concentrations of TACs. First, TACs used in the formulation of the cleaning agents may be directly emitted during and after use. Second, TACs may be formed by reaction of ozone with primary components of cleaning agents, such as formaldehyde formed from ozone-terpene chemistry. And third, the production of the OH radical by ozone-terpene chemistry can lead to the formation or destruction of TACs that originated from other sources. Thus, it is important to better understand the primary emissions from cleaning products and air fresheners and the possible interactions of ozone with constituent chemicals.

To address these issues, the research described in this report was undertaken. The project was organized into four tasks.

First, a critical review and synthesis of the existing literature was conducted. At the time the project started (2001) there already existed a substantial amount of information regarding the chemical constituents of cleaning agents (e.g., see Gosselin et al., 1984; Wolkoff et al., 1998; Salthammer, 1999; Zhu et al., 2001, and references therein). There was much less literature available on indoor chemical reactions between constituents of cleaning agents and ozone (e.g., see Weschler and Shields, 1997b; Weschler, 2001; Wolkoff and Nielson, 2001). Under Task 1 of the project, we prepared a critical review of the relevant literature. That review is presented as §2 of this report.

The second task entailed measuring the VOC composition and primary emissions of a set of common cleaning products and air fresheners. A multistage selection process was devised, focusing on widely available consumer products that contained chemicals in one of two categories: toxic VOCs such as ethylene based glycol ethers (which are regulated as TACs) and terpenes (which are known to react rapidly with ozone to form TACs such as formaldehyde). A shelf-survey was conducted in five major retail outlets in the San Francisco Bay Area to identify commonly available products. Fifty products were selected from a total of almost three hundred as possibly containing and emitting the compounds of interest to this study. Through consultation with ARB, we selected 21 cleaning products and air fresheners to be screened for their emissions of VOCs. The VOC constituents of these products were determined through laboratory measurements. Six of these products were then selected for further testing, in which emissions and concentration profiles of target analytes were determined during and after simulated-use in a room-scale chamber. The methods and results for this task are presented in §3 of this report. Important details are reported in three appendices. Appendix A presents the shelf-survey results. Appendix B contains the composition-screening data. Appendix C archives data collected during the simulated-use experiments.

In the third task, our objective was to develop new experimental data regarding the nature and quantity of reaction products when certain cleaning products and air fresheners are exposed to ozone. This investigation was motivated by four observations: certain cleaning agents contain

high levels of terpenes; elevated ozone levels can occur indoors; ozone reacts rapidly with terpenes; and the products of ozone-terpene chemistry include OH (a highly reactive radical), formaldehyde (a TAC), and secondary particulate matter (a regulated ambient air pollutant). Two complementary experimental approaches were employed. One entailed the use of a continuous flow, bench-scale reaction chamber. The second approach was based on simulated product use in a room-scale chamber with controlled ozone addition. In these studies, which are presented in §4, three products were tested, a pine-oil based general-purpose cleaner, an orange-oil based general-purpose degreaser, and a scented-oil plug-in air freshener. Appendices D and E archive the detailed experimental data generated in the bench-scale experiments and the simulated-use experiments, respectively.

In the fourth task, we interpreted the new experimental results in combination with the literature review to assess their overall significance for determining whether elevated air pollutant exposures might occur indoors as a result of the use of cleaning products or air fresheners, with and without exposure to ozone. The specific goal was to provide important information about several key points: the VOC constituents that are emitted from certain cleaning products and air fresheners, with and without exposure to ozone; the levels of those constituents under a realistic range of conditions of key variables; and the factors that substantially influence the constituent levels. This task was carried out by mathematical modeling of several exposure scenarios, utilizing new data collected in the experiments conducted in Tasks 2 and 3. The methods employed in this effort and the results are presented in §5.

A summary of all of the research carried out in this project is presented in §6. In §7, we provide recommendations for future research. Key experimental data are presented in tables and figures throughout the body of the report; however, extensively detailed data are presented in appendices.

2. REVIEW: EXPOSURE TO PRIMARY AND SECONDARY AIR POLLUTANTS ASSOCIATED WITH USE OF CLEANING PRODUCTS AND AIR FRESHENERS

2.1. Introduction

The cleaning of buildings and their contents is a major human activity that aims to promote hygiene, aesthetics, and material preservation. In the United States, out of a total working population of 128 million, three million people are employed as “janitors and cleaners,” or as “maids and housekeeping cleaners” (US Department of Labor, 2001). From activity pattern surveys, it is estimated that US adults devote an average of 20-30 minutes per day to house cleaning (Wiley et al., 1991). In addition, among California adults, 26% reported that they were near or used cleaning agents on the day on which they were surveyed and 31% reported that they were near or used scented room fresheners (Jenkins et al., 1991).

Despite the large overall effort devoted to these activities, relatively little scientific evidence documents the efficacy of building cleaning practices. Common themes in the literature include the effectiveness of vacuuming and other processes for controlling allergens (Hegarty et al., 1995; Woodfolk et al., 1993; Vaughan et al., 1999) and lead-contaminated dust (Ewers et al., 1994; Liroy et al., 1998). Studies have explored the role of disinfectants in cleaning agents on limiting the spread of infectious disease (Bloomfield and Scott, 1997; Josephson et al., 1997; Rusin et al., 1998). Only a few published studies have considered general cleaning efficacy (Schneider et al., 1994; Franke et al., 1997; Nilsen et al., 2002) or the beneficial attributes of cleaning products (Olson et al., 1994; Jerrim et al., 2001; Jerrim et al., 2002).

While there are substantial perceived benefits of cleaning, there are also risks. One set of concerns arises because cleaning products contain volatile organic compounds (VOCs) that contribute to urban or regional photochemical smog. The California Air Resources Board has adopted regulations to reduce atmospheric emissions from consumer products, including cleaning products and air fresheners (CARB, 2001). Cleaning may also pose risks to cleaners and to building occupants. Wolkoff et al. (1998) have summarized the spectrum of such concerns. These include irritation and other health hazards owing to inhalation exposures to cleaning-product constituents, exposures to dust and other particulate matter suspended during cleaning activities, and the production of secondary pollutants owing to the reaction of unsaturated organic compounds with oxidants such as ozone and nitrogen oxides.

This section of the report provides a critical review of the literature, exploring the nature and likely significance of air pollutant exposures among building occupants, including cleaning personnel, resulting from the use of cleaning products and air fresheners in homes and in nonindustrial workplaces. We emphasize chemical exposures resulting from the volatile constituents of cleaning products, considering both primary emissions from the cleaning products themselves and the formation of secondary pollutants caused by the interaction of cleaning product constituents with other reactive species. Our approach utilizes key principles and tools from the applied physical sciences — mass conservation, reactor models and analysis of kinetic systems — to explore the causal events linking cleaning product use with inhalation exposure to air pollutants.

2.2. Cleaning Products and Air Pollution

2.2.1 Emissions and inhalation intake

Because of their potential contributions to urban photochemical smog, product manufacturers and air quality regulators have estimated organic compound emissions from the

use of cleaning products. Table 2.1 presents summary data for California. The total estimated emissions of 32 tonnes d⁻¹ corresponds to about 1 g per person per day for the entire state's population. Emissions of reactive organic gases (ROG) from the sum of indoor and outdoor sources are estimated to be much larger, about 2400 tonnes d⁻¹ for the state (CARB, 2003).

Although cleaning agent use causes a small portion of total organic compound emissions, the health consequences from this usage are expected to be disproportionately larger than the emissions. This reflects the fact that the proportion of emissions inhaled is much higher when those emissions occur in buildings rather than outdoors. The relationship between inhalation and emissions is quantified through the *intake fraction* (Bennett et al., 2002), which is defined as the incremental pollutant mass inhaled per unit pollutant mass emitted. Typical intake fractions for emissions to outdoor air are in the range 10⁻⁶ to 10⁻³, whereas typical intake fractions for emissions into indoor air are in the range 10⁻³ to 10⁻¹ (Lai et al., 2000). Thus, the inhalation exposure from the 32 tonnes d⁻¹ of organic compounds emitted indoors from cleaning product use is expected to be of the order of (10⁻³-10⁻¹) × 32 × 10³ kg d⁻¹, corresponding to ~ 30-3000 kg d⁻¹, summed over the entire California population. This is of similar scale to the estimated inhalation exposure from organic compounds emitted outdoors from all sources combined, (10⁻⁶-10⁻³) × 2400 × 10³ kg d⁻¹, which corresponds to ~ 2-2000 kg d⁻¹, again summed over the entire California population.

It is important to appreciate that only a portion of the organic compounds emitted from cleaning products pose direct health concerns because of their toxicity (which varies among species over many orders of magnitude). Given a typical intake fraction of 10⁻² for airborne contaminant releases in buildings, the emissions of 1 g d⁻¹ person⁻¹ of organic compounds from cleaning product use would be expected to cause an average mass inhaled of ~ 10 mg (10000 µg) d⁻¹ person⁻¹, provided that most of the release occurs indoors. Depending on species toxicity, this average burden is high enough to be of potential concern. For example, “no significant risk levels” (NSRLs) have been established for inhalation exposure to some chemicals known to cause cancer by the State of California (OEHHA, 2003). These levels are set at a value such that lifetime exposure at that value would increase the estimated risk of cancer by 10⁻⁵. Sample NSRLs are 7 µg d⁻¹ for benzene, 40 µg d⁻¹ for formaldehyde, and 14 µg d⁻¹ for tetrachloroethylene. If even a small proportion, i.e. 0.1-1%, of the inhaled mass of organic compounds from cleaning products were as toxic as these compounds, the average exposure would approach levels of concern. Furthermore, inhalation exposures undoubtedly vary broadly across the population, with those who are regularly engaged in cleaning activities experiencing larger exposures than those who do not. This means that the risks to many individuals are likely to be much higher than the average risks throughout the population. In summary, this broad perspective provides some basis for concern about the potential adverse health consequences of inhalation exposure to cleaning agents.

2.2.2 Inhalation pathways

As summarized in Table 2.2, the use of cleaning products and air fresheners can influence inhalation exposure to air pollutants by several distinct mechanisms. Volatile constituents of the products can enter the gas phase during or after use. But nonvolatile constituents can also be inhaled, either because the cleaning process or air-freshener use itself releases liquid or solid particulate matter into the air or because residual cleaning materials are later suspended, for example through abrasion and wear. In a study that examined the inhalation concentrations of constituents found in a surrogate air freshener, fragrance constituents associated with airborne

particles accounted for approximately 47% of the adult and 72% of the child exposures in the breathing zone during the first minute after product use of an aerosol spray (Rogers et al., 2005). In addition, secondary pollutants are also of concern: the use of cleaning products or air fresheners can be accompanied by reactions in water (Shepherd et al., 1996), on surfaces (Webb et al., 2002; Pommer, 2003; Fick, 2003), or in the air (Weschler and Shields, 1999; Wainman et al., 2000), which can affect the indoor concentrations of air pollutants. Although this report focuses on air pollutants resulting directly or indirectly from the volatile components of cleaning products or air fresheners, the array of exposure routes of potential concern is broader.

2.3. Direct Evidence of Health Hazards

The medical, occupational, and environmental health literature contains many reports documenting cleaning related inhalation hazards (ingestion or dermal contact hazards are not considered in this review). The reports on inhalation hazards can be divided into those based on the mixing of cleaning products and those focusing on hypersensitivity responses associated with product use. This section summarizes findings from such studies with a view toward glean what these studies tell us about the broader issue of inhalation exposure to air pollutants from cleaning products.

2.3.1 Accidental poisonings associated with inappropriate mixing of cleaning agents

The mixing of certain types of cleaning products can generate hazardous fumes sufficient to cause those exposed to seek medical attention. Table 2.3 summarizes thirteen reports published during the past four decades documenting such episodes. Common throughout these reports is the use of bleach or other product containing hypochlorite (OCl^-) as an active ingredient. The mixing of bleach with ammonia-based cleaners causes the production of chloramines (NH_2Cl and NHCl_2) and possibly ammonia (NH_3) that can volatilize. In some cases, bleach has been mixed with an acid-based cleaner, which could cause the release of gaseous chlorine (Cl_2) or hypochlorous acid (HOCl).

In each of the case reports, one or more subjects sought medical attention for acute respiratory symptoms. Some subjects required no treatment and many others recovered within days. However, in several cases, ongoing respiratory-health impairment resulted from the exposure. One case led to a fatality (Cohle et al., 2001), although the subject had an undiagnosed preexisting condition possibly contributing to the outcome.

In total, this literature makes a compelling case that acute inhalation hazards can result from improper use of cleaning products. Recognizing this, it is common for manufacturers to print labels on cleaning products warning consumers to avoid mixing different products. A recent study suggests that only a small fraction of consumers read cleaning-product labels (Kovacs et al., 1997). The continuing appearance of case reports in the medical literature is clear evidence that the printed warnings have not eliminated the hazard of mixing. Furthermore, the number of total incidents is likely much larger than the published case reports. For example, Mrvos et al. (1993) cite information from the American Association of Poison Control Center's National Data Collection System, which reported more than 7000 exposures to chlorine or chloramine gas in the US in 1990. According to these authors "a large majority are likely to be in-home exposures resulting from the incorrect mixing of cleaning products." Extrapolating from the evidence summarized in Table 2.3, a plausible concern is that people may experience inhalation exposure to strong acids or bases, or to strong oxidants, owing to even the proper use of cleaning products containing such irritants. For example, reactions between hypochlorite and commonly occurring

ppb levels of indoor ammonia may produce low concentrations of chloramines; similarly, reactions between hypochlorite and ppb levels of indoor nitric, hydrochloric or sulfuric acids may produce small amounts of gaseous Cl_2 or hypochlorous acid. However, evidence is lacking to quantify the potential for such chronic, low-level exposures, or to determine their significance.

2.3.2 Asthma, allergy, and respiratory irritation

A second category of cleaning-related, health-effects literature focuses on occupational asthma, allergy, and/or respiratory irritation as the outcomes of concern. Among the eighteen studies summarized in Table 2.4 are two main types: case reports and epidemiological investigations. Five of the six case reports identify carpet shampoo or a floor cleaner as the product responsible for the adverse health effect. In several cases a specific chemical agent is identified: ethanolamine, lauryl dimethyl benzyl ammonium chloride, or benzalkonium chloride. In one case, the subject did not directly use the cleaning product. Rather, his occupational asthma was attributed to exposure to a constituent of the floor cleaner used in his office while it was unoccupied (Burge and Richardson, 1994).

Compared with the case reports, epidemiological investigations are not as effective in identifying specific causes, but instead provide important information about the size of the affected population. Recent studies in Spain, Finland, Brazil, and several states in the US document an increased prevalence of occupational or work-related asthma among those employed as cleaners.

In contrast to the cases in Table 2.3, in only a few of the studies in Table 2.4 are the adverse effects clearly associated with product misuse. Overall, whether owing to misuse or not, the existence of at least 31 documents appearing in peer-reviewed, archival journals that implicate cleaning or cleaning products as a cause of respiratory health impairment suggests that cleaning product use deserves attention as a cause of air pollutant exposure.

2.4. Composition, Primary Emissions, and Inhalation Exposure

In this section, we explore the causal chain-of-events linking the use of cleaning products with inhalation exposure to the primary volatile constituents. The output parameters of interest are species-specific concentration (mass per volume) or mole fraction (moles of species per mole of air), exposure (defined here as the time integral of concentration encountered by an exposed person), and inhalation intake (defined here as species mass inhaled by an exposed person). Broadly, these output parameters depend on three classes of processes: emissions, dynamic behavior, and human factors.

As an illustration of the relationships among these variables, consider the following example. In a cleaning episode, 50 g of a product is used in a single-family residence over a period of 1 h. Assume that 1% of the product is a volatile air contaminant that is completely released at a uniform rate during the hour of use (i.e., the emission rate is 500 mg/h for 1 h). Furthermore, assume that the residence has a volume of 300 m^3 and a ventilation rate of 0.7 h^{-1} , representative values for the California housing stock (Wilson et al., 1996), and not unusual for the US. Assume that the indoor air mixes rapidly throughout the house so that the species concentration does not vary in space. Also, assume that the contaminant does not sorb or decompose in indoor air, so that the only removal mechanism is ventilation. (Sorption effects are considered in §2.4.2.) The concentration of the contaminant owing to cleaning product use under these conditions is presented in Figure 2.1(a). The peak concentration, which occurs at the end of the emission period, is 1200 $\mu\text{g m}^{-3}$. After use, the concentration decays exponentially

with a rate constant equal to the air-exchange rate. For an occupant of the building who is present throughout a 10-h period beginning with product use, the total exposure to the contaminant is represented by the time-integral of the concentration, which is $2380 \mu\text{g m}^{-3} \text{ h}$. The intake is the time integral of the exposure concentration multiplied by the breathing rate. For a constant breathing rate at a typical value of $0.5 \text{ m}^3 \text{ h}^{-1}$, the inhalation intake would be $1190 \mu\text{g}$. The individual intake fraction for this one exposed individual is the intake divided by the mass released, i.e. 0.0024. With n occupants so exposed, the total intake fraction would be $0.0024n$.

2.4.1 Emissions

Emissions of primary constituents depend on product composition. Table 2.5a identifies volatile constituents of cleaning products or air fresheners that have been reported in the literature and that are listed by California in Proposition 65 and/or as Toxic Air Contaminants (TACs). Also indicated, where available, are inhalation intake rates or concentration levels that would indicate a threshold of concern for assessing health risk associated with chronic exposure. For those occupationally involved in cleaning, regular repeated exposures could lead to chronic health concerns. Even for less frequent episodic exposures, the time-weighted average exposure concentration over an extended period could be compared with the information presented in Table 2.5a to make a preliminary evaluation of the potential risk.

The product compositions reported in Table 2.5a are compiled from worldwide literature, and it is not known if these products were available in California. Furthermore, it should be noted that the publication dates of the cited studies in Table 2.5a extend back to 1987, and the median citation date in this table is 1992. Composition of consumer products may change with time owing to varying conditions in the marketplace and to regulations. One potential regulatory contributor is the 1990 US Clean Air Act Amendments (Hodgson and Levin, 2003), which have led to regulatory action to limit the level of photochemically reactive VOCs in consumer products so as to reduce ambient ozone concentrations. California adopted regulations for the chemical composition of consumer products, including cleaning products, beginning in 1991, and amended several times since (CARB, 2005a). These regulations restrict the total level of reactive VOCs in products. These regulations also restrict the use of methylene chloride, perchloroethylene, and trichloroethylene in certain types of consumer products. Another potential regulatory contributor is the Montreal Protocol, which restricts the use of chemicals that contribute to the depletion of stratospheric ozone. Among the chemicals listed in Table 2.5a, carbon tetrachloride and 1,1,1-trichloroethane are regulated as ozone-depleting substances (<http://www.epa.gov/ozone/ods.html>). A further potential contributor is California's Proposition 65, which creates a duty-to-warn requirement: "no person in the course of doing business may knowingly and intentionally expose any individual to Prop. 65-listed chemicals without first giving clear and reasonable warning to such individual." (Carrick, 1998). Proposition 65 was adopted in California in 1986, and it is reasonable to expect that the composition of some products sold in California may have changed to remove or reduce their content of chemicals that appear on the Proposition 65 list, because of the duty to warn.

Additional evidence about the presence of toxic air contaminants in cleaning products can be inferred from organic gas emission inventories prepared for the California Air Resources Board. In February 2003, ARB released an updated emission inventory and speciation profile for consumer products, "based on sales and composition data provided by manufacturers in the ARB's 1997 Consumer Products Survey"

(<http://www.arb.ca.gov/ei/speciate/cprodsactgsprof.htm>). Table 2.5b presents estimated mass emission factors for seven classes of cleaning products and for 20 chemicals that are included in the 1999 ARB Toxic Air Contaminants Identification Program (<http://www.arb.ca.gov/toxics/id/id.htm>). By far the chemicals with the highest rates of emissions from these products are 2-butoxyethanol (4,200 kg d⁻¹) and isopropyl alcohol (3,950 kg d⁻¹). Note that isopropyl alcohol belongs to Category IIb in the TAC identification list, which indicates that this substance has not been identified as a toxic air contaminant. It is noteworthy that 12 chemicals are common to both lists; this represents a majority of the 21 entries in Table 2.5a and also a majority of the 20 entries in Table 2.5b.

The lists in Tables 2.5a and 2.5b do not represent all toxic constituents of potential concern. For example, 4-nonylphenol and nonylphenol ethoxylates are used in disinfecting cleaners, all purpose cleaners and spot removers (Betts, 2003). Reflecting their widespread use, they have recently been reported to be present in the dust and air of each of 120 homes sampled in the Cape Cod region of Massachusetts, with airborne concentrations of 4-nonylphenol ranging from 21 to 420 ng m⁻³ (Rudel et al., 2003). These compounds are of concern because of their ability to mimic female estrogen hormones. However, neither California nor the US EPA has yet to establish exposure guidelines for chemicals based on potential hormonal activity. An attempt to list all such chemicals is beyond the scope of this review.

A second important factor affecting emissions is the concentration of the volatile constituent in the cleaning product. Some composition and concentration information is available in material safety data sheets (MSDS) from product manufacturers. A few published studies also have reported composition data. For example, Zhu et al. (2001) tested Canadian consumer cleaning products and studied in detail 2-butoxyethanol (BE, C₆H₁₄O₂), a glycol ether. For five water-based products, the following percentage concentrations of BE were reported: all-purpose cleaner, 3.72%; glass and surface cleaner (clear), 0.87%; glass and surface cleaner (blue), 0.50%; antibacterial glass and surface cleaner, 0.83%; and lemon fresh and antibacterial spray, 1.28%.

A third factor affecting emissions is the product usage pattern, including the quantity of product used and the frequency of application. These could be considered human factors, and they are discussed in §2.4.3. In addition, the manner of application can influence the timing of emissions, and possibly the total amount emitted. For a single application, product volume times the concentration of the volatile species in the product determines the maximum total release. Depending on the mode of application, all or only part of this mass may be emitted (Wooley et al., 1990). For example, if a floor-cleaning product is diluted in water, applied with a mop, and then the floor is rinsed, some of the volatile constituents may be poured down the drain with the dirty wastewater. In addition to influencing the total amount released, the mode of use along with the physicochemical properties of the volatile constituent can affect the timing of emissions. Emission studies suggest that glycol ether release from aqueous cleaning products occurs slowly, over periods of hours or even a few days after application (Gibson et al., 1991; Zhu et al., 2001). If generally true, such behavior would have the effect of reducing exposures during cleaning activities, but increasing exposures to building occupants following cleaning.

2.4.2 *Dynamic behavior*

Once primary constituents are emitted into indoor air, the resulting concentrations, exposures, and inhalation intake depend on the dynamic behavior of the species in indoor air. Factors influencing the species behavior include ventilation, mixing within a room, mixing

between rooms, homogeneous and heterogeneous transformations, sorptive interactions on surfaces, and active air cleaning. This section presents key aspects of most of these factors. Active air cleaning is briefly discussed in §2.4.3, and the role of transformation processes is addressed in §2.5.

Ventilation is a major factor influencing the concentrations of indoor pollutants. Commonly, it is expressed in terms of an air-exchange rate, λ , which is the volume flow rate of air out of a building divided by the volume of air contained within the building. Murray and Burmaster (1995) have analyzed measurements of λ for 2844 US households (not a statistically representative sample). These data are reasonably well described by a lognormal distribution with a geometric mean (GM) of 0.53 h^{-1} and a geometric standard deviation (GSD) of 2.3. Persily (1989) reported on extensive ventilation measurements in 14 office buildings across the US. The time-average values of λ across this sample of buildings are well described as lognormal with a GM of 0.73 h^{-1} and a GSD of 1.8.

In the example presented at the beginning of §2.4, we assumed that indoor air was well mixed. Spatial variability in concentrations can occur, especially when species are emitted from localized sources. One quantitative indicator is the characteristic mixing time, τ , defined as the period required for an instantaneous point release in an unventilated room to disperse such that the relative standard deviation among local concentrations is less than 10%. Baughman et al. (1994) measured τ in a 31-m^3 room under natural convection flow conditions and found that it varied from ~ 10 min with strong convection sources to ~ 90 min under thermally quiescent conditions. Drescher et al. (1995) measured τ to be 2-15 min in the same room for a variety of forced flow conditions. Under conditions where $\tau \ll \lambda^{-1}$ and where the exposure duration is much longer than the release time, the well-mixed approximation should describe exposure conditions reasonably well.

The failure of the well-mixed approximation would be expected to be most acute for estimating peak exposure concentrations for people who are engaged in cleaning activities. Girman et al. (1987) reported on a directly relevant experiment in which a researcher used a paint stripper that contained methylene chloride (CH_2Cl_2) to remove paint from a test panel in a 20-m^3 chamber. The time-dependent CH_2Cl_2 concentration was measured in the breathing zone of the researcher as well as in the center of the chamber during 90 min of activity. At a low air-exchange rate (0.6 h^{-1}), the personal exposure of 2400 ppm-h was very similar to the inferred exposure based on the room-air sampler, 2350 ppm-h. At a high air-exchange rate (3.2 h^{-1}), the personal exposure was about 20% higher than determined from the room air sampler (1120 ppm-h vs. 920 ppm-h); the short-term peak personal-exposure concentration was about 35% higher than the room-air peak (1320 vs. 970 ppm).

Transport between rooms can also affect concentrations and exposures. For people doing cleaning, interzonal transport can reduce concentrations in the room in which they are working, but for occupants of other rooms of the building, it is a vehicle for exposure that might not otherwise occur. Multizone modeling tools have been developed to predict interzonal flows based on information about the ventilation system, interzonal leakage, temperature, and wind conditions (Haghighat and Megri, 1996 and references therein). Although only a limited set of buildings have been examined with these tools, a few generalizations can be made. In residences, open internal doorways and the operation of central-air systems promotes rapid mixing. On the other hand, when the forced air system is off, transport between rooms separated by a closed doorway can be slow. In commercial buildings, air handling systems commonly

recirculate ~80 to 90% of the air flowing through them, promoting mixing throughout the zone served. However, large buildings may be served by multiple air handling units and little is known about the transport of species from one air-handler zone to another. Likewise, little is known about interroom transport in public buildings in which there is no forced recirculating flow, either by design or because the fans are not operating.

The sorptive interactions of cleaning product constituents with indoor surfaces may strongly influence time-dependent concentration fields, and therefore exposures. Species having low or moderate vapor pressure or high polarity may preferentially partition onto the surfaces or into the bulk media of materials found indoors. Sorptive uptake on surfaces has the effect of reducing peak concentrations from episodic uses. To the extent the interactions are reversible, subsequent desorption could serve as a contaminant source after the emissions would otherwise have been purged from the space. Sorptive interactions have emerged as an important indoor-air-quality research subject during the past few decades. Table 2.6 catalogs the literature on sorptive interactions involving constituents of concern in cleaning products and materials used indoors. Despite these extensive studies there remain unresolved issues, including the degree to which sorption is reversible vs. irreversible, the extent to which sorption is a surface phenomena vs. one in which internal mass transport may be limiting, and the effects of changing environmental conditions (temperature, humidity) on sorptive uptake or release.

Figure 2.1(b) illustrates the potential significance of sorption in influencing concentration profiles. The conditions are the same as for Figure 2.1(a): episodic release of 500 mg of a gaseous pollutant during a one-h cleaning activity in a single-family dwelling. In this case, completely reversible sorption is added to the governing material balance equation. The simulation model follows the pioneering work of Tichenor et al. (1991), and the rate constants for sorptive uptake and desorption are based on data from Sparks et al. (1999) for 2-(2-butoxyethoxy)ethanol interactions with carpet and gypsum board. Results from two simulations are shown. In one, the initial sorbed mass is assumed to be zero, which would correspond to the first use of the cleaning product in the space. In the second, the application cycle is repeated at weekly intervals for one year. The sorbed contaminant mass increases weekly, approaching a steady-state level by the end of the simulated period. The fractional difference between these simulations is small during and shortly after product use. However, the accumulation of sorbed mass in the second simulation leads to a much higher background concentration during the post-cleaning period: the average concentration for days 2-7 is $1.1 \mu\text{g m}^{-3}$ in the first case and $12 \mu\text{g m}^{-3}$ in the second. Comparing the nonsorbing case (Figure 2.1(a)) with the repeated-cycle sorbing case, there are two large differences. Sorption greatly reduces the peak concentration, so that exposure (the time-integral of concentration) during the first 10 h beginning with product use decreases from $2380 \mu\text{g m}^{-3} \text{ h}$ without sorption to $470 \mu\text{g m}^{-3} \text{ h}$ with sorption. However, the persistent background from desorption during the post-cleaning period compensates for this difference: the potential exposure during hours 10-168 is zero without sorption, but $1880 \mu\text{g m}^{-3} \text{ h}$ with sorption. To the extent that effects are related to peak concentrations, sorption may be beneficial overall by reducing peak exposures during cleaning activities. However, if occupancy is much lower during cleaning than at other times, then reversible sorption could cause a much higher population intake of primary pollutants than would occur for a nonsorbing species.

2.4.3 Human factors

Emissions, concentrations, exposures, and intakes of hazardous air pollutants from cleaning product use all depend in part on human factors. One set of human factors influencing

emissions is the characteristics of use: frequency, amount, and manner of application. Only a few published studies have looked at cleaning product usage by consumers. Weegels and van Veen (2001) studied the usage of dishwashing liquid, all-purpose cleaner, toilet cleaner, and hair spray in 30 households in The Netherlands. For all-purpose cleaners, they found an average contact frequency of 0.35 per subject per day, a mean duration of 20 min per contact, and an average product usage of 27 g per contact. Kovacs et al. (1997) found that consumers preferred cleaning products with a pleasant scent. They also observed that less of a scented product (either pleasant or unpleasant) was used for cleaning than an unscented product.

A second important human factor linking exposure to intake is breathing rate. Adams (1993) measured breathing rates of 200 individuals across a range of age and activity levels. At rest, average breathing rates were in the range of $0.4\text{--}0.6\text{ m}^3\text{ h}^{-1}$, depending on gender, age (child vs. adult), and position (prone, seated, or standing). The average breathing rate for adult females performing housework was $1.0\text{ m}^3\text{ h}^{-1}$. Adult males were not monitored performing this activity. Marty et al. (2002) have estimated that the population mean breathing rate for adults is $0.23\text{ m}^3\text{ kg}^{-1}\text{ d}^{-1}$, which corresponds to $0.67\text{ m}^3\text{ h}^{-1}$ ($16\text{ m}^3\text{ d}^{-1}$) for a 70 kg subject.

A third set of human factors addresses the timing of cleaning activities relative to occupancy, how the building is operated during and after cleaning, and the use of protective measures to limit exposure and intake. It should be clear from Figure 2.1 that exposure can be affected by the level of occupancy during cleaning. Exposures are minimized by conducting cleaning activities while occupancy is at a minimum, and as far in advance as possible of the next period of heavy occupancy. In addition, it is beneficial to maintain building ventilation, especially during cleaning, but also afterward. In private residences, window opening can be used to increase ventilation rates (Howard-Reed et al., 2002). Enhanced ventilation may incur costs, especially when the ambient temperature is hot or cold. In principle, these costs could be weighed against the benefit of reduced exposures; however, information is inadequate to do so objectively. Finally, both personal respiratory protection measures and indoor air cleaning devices could be used to reduce exposure and intake. Devices commonly used, such as disposable face masks and recirculating air filters, are designed to be effective against particulate matter but not against volatile organic compounds. Activated carbon sorbents are used for personal protection in hazardous material handling. Air cleaning devices that use activated carbon have also been investigated in laboratory studies (VanOsdell et al., 1996). However, we found no evidence of sorbents being used to limit exposure to cleaning product constituents.

2.5. Reactive Chemistry and Secondary Pollutants

2.5.1 Reactions with ozone

Cleaning product and air freshener constituents can react with oxidants to generate secondary pollutants. Ozone is a common initiator for indoor gas-phase oxidation processes. Reactions of ozone with constituents containing unsaturated carbon-carbon bonds are much faster, and serve as a larger source of secondary pollutants, than reactions with constituents containing only saturated carbon-carbon bonds. Table 2.7 lists constituents of cleaning products and air fresheners with C=C bonds. Most of these potentially reactive chemicals are terpenes (e.g., α -pinene, d-limonene, myrcene) or terpene-related compounds (e.g., linalool, α -terpineol and linalyl acetate). Their inclusion in cleaning products reflects the favorable odor characteristics and solvent properties of terpenoids. Some of the entries in Table 2.7 have not been explicitly reported but are inferred to be present in cleaning products or air fresheners since they are known constituents of oils or scent formulations used in such products (e.g., α -terpinene

found in pine oil; selected sesquiterpenes found in waxes, orange oil and lemon-peel oil). Not only are there differences in ozone reactivity rates between unsaturated constituents (Table 2.7) and saturated ingredients (most of the compounds listed in Table 2.5), but also there are substantial differences among the unsaturated constituents themselves. Table 2.8 lists 2nd order rate constants for reactions between the compounds in Table 2.7 and ozone. The compounds are rank-ordered based on their 2nd order constants for reaction with ozone. These ozone rate constants span more than 4 orders of magnitude.

2.5.2 Reactions with OH and NO₃

Hydroxyl radicals and nitrate radicals are other oxidants that may be present indoors at sufficient concentrations to produce significant quantities of secondary pollutants. Indoor hydroxyl radicals are derived primarily from ozone/alkene reactions (Nazaroff and Cass, 1986; Weschler and Shields, 1996; 1997a; Sarwar et al., 2002b), while indoor nitrate radicals result from the reaction between ozone and nitrogen dioxide (Nazaroff and Cass, 1986; Weschler et al., 1992; Sarwar et al., 2002a). Table 2.8 also lists the 2nd order rate constants for OH and NO₃ reactions with the compounds in Table 2.7. In contrast to the rate constants for reactions with ozone, those for the reactions with OH span a relatively narrow range, approximately an order of magnitude. The rate constants for reactions with NO₃ demonstrate variability that lies between these extremes, spanning approximately 3 orders of magnitude. There are many widely used unsaturated constituents of cleaning products whose rates of reaction with common indoor oxidants have not been reported in the literature. These include linalyl acetate, a common odorant (and a constituent of bergamot); and dihydromyrcenol, another common odorant (and a constituent of lavender).

2.5.3 Rate comparisons

For a gas-phase reaction between ozone and a cleaning constituent to have a meaningful impact in an indoor environment, the reaction must occur at a rate competitive with air-exchange rates or other removal processes (Weschler and Shields, 2000). Table 2.8 includes pseudo 1st order rate constants for the reaction of the unsaturated constituents with O₃, OH and NO₃ at oxidant concentrations that are representative of those expected near midday during the ozone season in certain indoor settings. These levels are 20 ppb for O₃ (Weschler, 2000), 5×10^{-6} ppb for OH (Sarwar et al., 2002b), and 1×10^{-3} ppb for NO₃ (Sarwar et al., 2002a). Note that the concentration of indoor O₃ is highly variable and depends on both the outdoor ozone level and the air-exchange rate; the concentrations of OH and NO₃ are similarly variable since they are derived from reactions initiated by O₃. The reactions of O₃ with most of the compounds in Table 2.7 are fast enough to be potentially significant in some indoor settings; the exceptions are the very slow reactions with camphene and longifolene. The reactions between O₃ and α -terpinene, terpinolene and the three listed sesquiterpenes are fast enough to have consequences even at air-exchange rates as high as 10 h⁻¹. At the OH levels anticipated in indoor settings, reactions between the compounds in Table 2.7 and OH are expected to be important only at lower air-exchange rates. Even the fastest of these reactions has a pseudo 1st order rate constant of just 0.16 h⁻¹ at an OH level of 5×10^{-6} ppb.

Most of the compounds in Table 2.7 have pseudo 1st order rate constants for reactions with NO₃ that are larger than the analogous rates with OH. Indeed, a number are faster than the analogous rates with O₃. Nitrate radical reactions are anticipated to be particularly important during air pollution episodes with simultaneously elevated NO₂ and O₃. For example, during 14

months of measurements at an office building in Burbank, CA several periods were recorded when indoor NO_2 exceeded 60 ppb while indoor O_3 simultaneously exceeded 30 ppb (Weschler et al., 1994). For similar reasons, NO_3 reactions may also take on added significance in indoor settings with unvented combustion appliances. Of particular note are the reactions of NO_3 with d-limonene ($k' = 1.1 \text{ h}^{-1}$), linalool ($k' = 1.0 \text{ h}^{-1}$), terpinolene ($k' = 8.6 \text{ h}^{-1}$), and α -terpinene ($k' = 16 \text{ h}^{-1}$).

2.5.4 Oxidation products

Atkinson and Arey (2003) reviewed the kinetics, mechanisms and products of gas-phase reactions between biogenic organic compounds — mostly terpenoids — and the oxidants O_3 , OH and NO_3 . Much of the reactive chemistry discussed in their paper is relevant to unsaturated cleaning constituents. The major difference is that photochemistry plays an important role in outdoor reactive chemistry, but normally makes only a negligible direct contribution indoors. Table 2.9 presents the general types of secondary pollutants produced by reactions between unsaturated cleaning compounds or air freshener constituents and O_3 , OH and NO_3 . These include free radicals, starting with stabilized Criegee biradicals (probably carbonyl oxides; see Kroll et al., 2002). Hydroperoxy and alkyl peroxy radicals warrant special comment. Their lifetimes may be longer indoors than outdoors and their fate indoors may also be altered. Under indoor conditions that produce HO_2 and RO_2 , the concentration of NO tends to be extremely low, because the reaction between O_3 and NO is fast, and because negligible NO is produced by indoor photodissociation of NO_2 (Weschler et al., 1994). Hence, the NO destruction pathways of HO_2 and RO_2 are less important indoors than is common outdoors. Modeling studies indicate that indoor HO_2 can easily reach low ppt levels, while indoor CH_3O_2 can exceed 10 ppt (Sarwar et al., 2002a).

Other short-lived, highly reactive species include peroxyhemiacetals and secondary ozonides. Many of the oxidation products are stable compounds with one or more oxygen-containing functional groups ($-\text{C}=\text{O}$, $-\text{C}-\text{OH}$, $-\text{COOH}$, $-\text{C}-\text{NO}_2$). As a consequence of these substituent groups, such products absorb radiation in the near-UV range and are susceptible to photodegradation in outdoor air. However, in indoor environments the removal rate by this pathway is small, implying longer lifetimes indoors (especially if the products are sorbed to indoor surfaces). Some of the oxidation products have low vapor pressures and partition between the gas phase and airborne particles, contributing to the growth of secondary organic aerosols (SOA). The increase in the mass concentration of indoor SOA as a consequence of such reactions can be in the range of 10 to 100 $\mu\text{g m}^{-3}$ (Weschler and Shields, 1999, 2003; Wainman et al., 2000; Weschler, 2003a; Sarwar et al., 2003, 2004; Fan et al., 2003, 2005; Leungsakul et al., 2005).

Some of the oxidation products have extremely low odor thresholds (e.g., selected unsaturated aldehydes have thresholds below 50 ppt, while selected aldehydes and carboxylic acids have thresholds in the low ppb range; see Devos et al., 1990). Many products derived from oxidation of the compounds listed in Table 2.7 are known or anticipated to be irritating (e.g., certain aldehydes, peroxides, hydroperoxides, secondary ozonides, mono- and dicarboxylic acids). Both acrolein and formaldehyde are eye irritants and are listed as California TACs with acute reference exposure levels (RELs) for a one-hour exposure of 0.19 and 94 $\mu\text{g m}^{-3}$, respectively. Investigators have reported increased eye-blink frequency as a consequence of exposure to the products of ozone/limonene reactions at realistic precursor concentrations (Klenø and Wolkoff, 2004; Klenø-Nojgaard et al., 2005). Laumbach et al. (2005) have reported nasal

effects resulting from short-term human exposure to a mixture that contained α -pinene and d-limonene oxidation products. Tamás et al. (2005) have demonstrated, over a range of realistic concentrations, that perceived air quality is significantly poorer when ozone and limonene are present together in a room compared to conditions in which only ozone or only limonene is present.

Exposure to acetaldehyde, acrolein, formaldehyde and glutaraldehyde pose long-term hazards to the respiratory system and are listed as TACs with chronic RELs of 9, 0.06, 3 and $0.08 \mu\text{g m}^{-3}$, respectively. Certain air oxidation products of d-limonene have been identified as contact allergens (Karlberg et al., 1992; 1994; Nilsson et al., 1996), and some of these same compounds have been found in the mix of products resulting from ozone-initiated oxidation of d-limonene (Clausen et al., 2001). An IARC working group has recently concluded that formaldehyde is carcinogenic to humans, based on both human and animal findings (Cogliano et al., 2005). Some of the other oxidation products (e.g., acrolein, certain organic nitrates, and SOA) are suspected carcinogens. Taken together, circumstantial evidence suggests that the products of ozone-initiated indoor chemistry contribute in a meaningful way to the ill health associated with ambient ozone (Weschler, 2004a and 2004b). However, much more work is required to define the health consequences resulting from exposure to such products (Weschler et al., 2005). Indeed, for most of the products of ozone-initiated indoor chemistry, detailed toxicological information is still not available. Also, many of the reaction products are “stealth pollutants”; i.e., they are difficult to detect and are often overlooked in the sampling and analysis of indoor air (Weschler and Shields, 1997b; Wolkoff, and Nielsen, 2001; Carslaw, 2003). This is especially true for free radicals, other short-lived species, thermally labile compounds, and multifunctional products. Atkinson and Arey (2003) specifically mention hydroxy carbonyls, dihydroxy carbonyls, hydroxy nitrates and carbonyl nitrates as known products that are analytically challenging. A similar statement applies to certain organic peroxides formed from the reactions of monoterpenes with ozone (Docherty et al., 2005). Over the past ten years there have been advances in derivatizing and detecting higher molecular weight multi-functional products. However, these methods have not been routinely used in indoor air investigations. The “stealth” nature of some of the oxidation products further complicates attempts to make associations between such species and reported health effects.

Some of the first generation oxidation products of the compounds in Table 2.7 contain one or more unsaturated bonds. Examples include 4-acetyl-1-methylcyclohexene (ACM) and 3-isopropenyl-6-oxoheptanal (IPOH or endolim) from the oxidation of limonene and 5-methyl-5-vinyltetrahydrofuran-2-ol (MVT) from the oxidation of linalool. Such compounds tend to react with O_3 at rates slower than their parent compounds, but in some cases still fast enough to contribute to additional “secondary” product formation. Details for specific unsaturated products are further discussed in Calogirou et al. (1999a, 1999b), in the Atkinson/Arey review and in references cited therein. First generation oxidation products, including those with no unsaturated bonds, can react with OH and NO_3 . Hallquist et al. (1997) have reported rate constants for the reaction of OH and NO_3 with pinonaldehyde and caronaldehyde, oxidation products of α -pinene and Δ^3 -carene, respectively. However, such kinetic information is not available for most of the first-generation oxidation products of cleaning agent and air freshener constituents.

Reactions with OH and NO_3 also can be significant for primary cleaner or air freshener emissions with no unsaturated bonds. In studies of ozone (40 ppb) and a mixture of 23 volatile organic compounds, including d-limonene and α -pinene, the products included compounds that were not directly generated by reactions with ozone, but resulted from secondary reactions

between hydroxyl radicals and components of the initial mixture (Fan et al., 2003). Indeed, kinetic modeling of the mixture indicated that OH was responsible for 55 - 70% of the resulting formaldehyde and 20 - 30% of the secondary organic aerosol. Such reactions may reduce the airborne concentrations of Proposition 65 and TAC constituents listed in Table 2.5; however, the products may also be of concern. Reactions of the glycol ethers with OH and NO₃ warrant special comment since they are sometimes the major active ingredient of a cleaning product and are receiving increased scrutiny regarding their potential health effects. Consider, for example, the OH/2-butoxyethanol and NO₃/2-butoxyethanol reactions for which the 2nd order rate constants are 0.5 ppb⁻¹ s⁻¹ (Stemmler et al., 1996) and < 0.004 ppb⁻¹ s⁻¹ (Chew et al., 1998), respectively. For the typical indoor OH and NO₃ concentrations reported in Table 2.8, the resulting pseudo 1st order rate constant for either oxidant is less than 0.01 h⁻¹, too slow to be significant in terms of 2-butoxyethanol removal. However, the significance for product formation is not clear, as even small fractional conversion of 2-butoxyethanol could be of concern if the toxic potency of one or more of the products were high. Such products include ethylene glycol monoformate, butyl formate, propionaldehyde, 3-hydroxybutyl formate, butoxyacetaldehyde, and propyl nitrate (Stemmler et al., 1997). Hydroxyl radicals react up to four times faster with certain other glycol ethers than with 2-butoxyethanol (Aschmann et al., 2001).

2.5.5 Reactions on surfaces

Given their vapor pressures and polarities, many glycol ethers are anticipated to partition between the gas phase and indoor surfaces (see §2.4.2). Although the gas-phase oxidation of glycol ethers is severely limited by their airborne residence time, there is considerably more time for oxidation if these compounds are sorbed on surfaces. Indeed, oxidation processes initiated by ozone and even dioxygen (i.e., autoxidation) may be important on surfaces. The autoxidation of glycol ethers produces peroxides and hydroperoxides as primary products and alkyl poly(ethylene glycol) aldehydes, alkyl poly(ethylene glycol) formates, hydroxyaldehydes, and even formaldehyde as secondary products (Bodin et al., 2003). These processes have been the subject of considerable study since some of the products are irritants and skin sensitizers (Bodin et al., 2000; 2001; 2002; 2003).

Surface oxidation also may be important for other constituents of cleaning products and air fresheners. Laboratory studies of the reaction of ozone (Fick et al., 2002) or ozone and nitrogen oxides (Pommer, 2003) with α -pinene, Δ^3 -carene and limonene indicate that surface reactions, as well as gas-phase processes, are contributing to the removal of these terpenes; the effect was most pronounced for Δ^3 -carene. In buildings with mechanical ventilation systems, the particle filters present a potentially important site for surface oxidation processes to occur. As these filters load (i.e., collect particulate matter), the resultant surface area of the captured particles can become quite large (Weschler, 2003b). Such filters are typically located downstream of the mixing box, such that the air passing through them is a mixture of recirculated and outdoor air. During a cleaning event the recirculated air may contain high concentrations of compounds from Tables 2.5 and 2.7. Such compounds will, to a greater or lesser extent, partition between the airstream and the surface of the loaded filters. The mixed airstream contains a fraction of outside air (typically 10 to 20%), and ozone in this air can react with sorbed constituents, producing products that subsequently desorb into the supply air over an extended interval (Beko et al., 2005). This can further expose building occupants to oxidized constituents of cleaning agents and air fresheners. The importance of oxidation processes on a

filter surface is anticipated to grow as a filter loads. Surface oxidation of compounds found in cleaning agents and air fresheners, whether on surfaces within a room or within an HVAC system, is an area that has received little attention and warrants further investigation.

2.5.6 Influence of reactive chemistry

Reactive chemistry influences the dynamic behavior and fate of selected primary emissions and generates secondary pollutants, many of which would not exist indoors in the absence of such chemical transformations. Figure 2.2 illustrates the potential significance of such chemistry on concentration profiles. The conditions are the same as for Figure 2.1(a): episodic release of 500 mg of a gaseous pollutant during a one-h cleaning activity in a well-mixed, single-family dwelling. In this case, a chemical reaction between the volatile constituent and ozone is added to the governing material balance equation. The assumed indoor concentration of ozone is constant at 20 ppb. The assumed 2nd order rate constant is $5.2 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$, similar to the value for the ozone/limonene reaction (Table 2.8). Figure 2.2 depicts both the concentration of the volatile constituent and the concentration of a hypothetical product. The latter has been calculated assuming the stoichiometry is one molecule of product formed per molecule of reactant consumed, and the product is nonsorbing and has the same molecular weight as the reactant. With reactive chemistry, the concentration of the volatile constituent reaches a peak value of $1020 \mu\text{g m}^{-3}$ compared to $1200 \mu\text{g m}^{-3}$ in the nonsorbing, no-chemistry case (Figure 2.1(a)). Whereas this peak occurs at the end of the emission period, the peak value for the hypothetical product ($250 \mu\text{g m}^{-3}$) occurs almost three quarters of an hour after the end of the emission period, 1.7 h after the beginning of the cleaning episode. This lag reflects the time required for reaction to proceed coupled with the fact that the volatile constituent continues to react and generate product even after its emission ceases and its concentration begins to decay. Thus, the hypothetical secondary product is more persistent than the primary volatile constituent. Six hours after the cleaning episode began, and 5 hours after the emission of the cleaning constituent ceased, the concentration of the hypothetical product is still at 12% of its maximum value.

In reality, ozone-initiated chemistry produces multiple products (Table 2.9), most of which have yields significantly less than unity. Formaldehyde is a known product for the reaction between ozone and several of the constituents listed in Table 2.7. If the reaction simulated in Figure 2.2 had a formaldehyde yield of 10%, similar to that for the ozone/limonene reaction (Grosjean et al., 1993), then this reaction would add $5.6 \mu\text{g m}^{-3}$ of formaldehyde to the room air at its maximum contribution. Secondary organic aerosols (SOA) are also known products for the reaction between ozone and many of the constituents in Table 2.7. If an SOA yield of 20% is assumed and the average molecular mass of the products contributing to SOA growth is assumed to be 150 g mole^{-1} , then the peak value of SOA added to the air as a consequence of this reaction would be $56 \mu\text{g m}^{-3}$. Some cleaners contain 15% pine oil, a mixture of primarily unsaturated terpenoids, some of which react with ozone even faster than limonene (e.g., terpinolene and α -terpinene). Such cleaning products have the potential to generate significantly higher concentrations of secondary pollutants than those shown in Figure 2.2.

The causal chain-of-events that links secondary pollutants with inhalation exposure is similar to that for primary pollutants and broadly depends on the same three classes of processes: emissions, dynamic behavior and human factors. However, ventilation and mixing times affect the dynamic behavior and fate of secondary pollutants in an added way since the residence times defined by these factors limit the time available for gas-phase transformation processes

(Weschler and Shields, 2000; Sorensen and Weschler, 2002; Weschler and Shields, 2003). Also, in considering human factors, it should be noted that some of the short-lived, highly reactive compounds (e.g, hydroxyl radicals, hydroperoxy radicals, alkyl peroxyradicals) may be too reactive to penetrate very far within the respiratory tract. On the other hand, for species such as α -terpinene that react with ozone at a relatively fast rate, there is the possibility that an inhaled mixture of ozone and the quickly reacting constituent may produce free radicals as the mixture travels along the respiratory tract. Many of the chemicals generated by O_3 , OH or NO_3 initiated oxidation processes are expected to be more irritating than their precursors since oxidized products are more polar, more water soluble, and are often more odorous and acidic. Although the products of nitrate radical chemistry may be of special concern, the current assessment of the role of NO_3 in indoor chemical transformations is based solely on modeling and inference from outdoor nighttime processes.

2.6. Conclusion

In this review, we have synthesized a diverse literature relevant to several key elements of air pollutant exposures associated with cleaning product and air freshener use. We have organized the information into a logical framework stressing the causal relationships among concentrations, exposures, and intake, and the many input variables upon which they depend. As we have demonstrated, there are strong parallels between exposure from cleaning product and air freshener use and the broader concerns of air pollutant exposures from indoor sources. Important data gaps remain to be filled before a fully satisfactory understanding can be gained of inhalation exposures associated with cleaning products and air fresheners. Key data needs include better information on product composition, human factors that affect use and exposure, mechanistic and kinetic details for reactions involving important constituents, and the potential health effects of the secondary pollutants. Although these gaps exist, mass conservation, reaction kinetics and mechanistic reasoning can be used to examine linkages between cleaning product and air freshener use and resulting pollutant exposures.

Table 2.10 provides a concise summary of the specific findings reported in §2.

Table 2.1. Estimated atmospheric emissions of volatile organic compounds from use of household and commercial cleaning products and air fresheners in California, 1997. ^a

Product	VOC emissions (tonnes/d)	per capita VOC emissions (mg d⁻¹ person⁻¹)
Carpet and upholstery care: cleaners and deodorizers	1.07	32
Spot removers	0.64	20
Fabric protectants	0.37	11
Floor care: wax, wax strippers, polish	5.6	170
General purpose cleaners	7.4	220
General purpose degreasers	2.1	64
Glass cleaners	3.4	100
Oven cleaners and metal polishes/cleansers	0.87	26
Bathroom cleaners: toilet bowl, tub, tile, and sink	0.74	22
Furniture waxes and polishes; dusting aids	2.4	71
Air fresheners	7.5	230

^a *Source:* CARB, 2003; per capita emissions based on 1997 population estimate of 33 million (<http://www.dhs.cahwnet.gov/hisp/chs/OHIR/Population/populationindex.htm>).

Table 2.2. Mechanisms by which use of cleaning products can influence inhalation exposure to air pollutants.

Mechanism	Examples
Volatilization	Formaldehyde from wood floor cleaning spray (Akland and Whitaker, 2000; Figure 4-11); glycol ethers from hard-surface cleaners (Zhu et al., 2001; Gibson et al., 1991)
Production of airborne droplets	Aerosol or pump-spray delivery of surface cleaning products; some spray droplets remain airborne instead of depositing (Fortmann et al., 1999; Roache et al., 2000)
Suspension of powders	Fine particulate matter from carpet freshener (Steiber, 1995); sodium tripolyphosphate from carpet cleaner (Lynch, 2000)
Suspension of wear products	Surfactants, film formers, complexing agents, acids and bases, disinfectants (Wolkoff et al., 1998; Vejrup and Wolkoff, 2002)
Inappropriate mixing	Chloramines from mixing household bleach and ammonia-based cleaners; chlorine gas from mixing bleach with acid-containing cleaner (see Table 2.3)
Chemical transformations	Chloroform release from chlorine bleach chemistry in laundry applications (Shepherd et al., 1996); terpene hydrocarbons plus ozone form OH radical (Weschler and Shields, 1997a), hydrogen peroxide (Li et al., 2002) and secondary particulate matter (Weschler and Shields, 1999; Wainman et al., 2000)
Altered surfaces	Nicotine release from walls following ammonia cleaner use in smoking environment (Webb et al., 2002); enhanced volatile organic emissions from wet linoleum (Wolkoff et al., 1995)

Table 2.3. Documented inhalation toxicity related to mixing of cleaning products.

Nature of Study	Products Mixed	Toxic Gas(es)	Outcomes	Ref ^a
Case reports (2)	NaOCl, vinegar, bleach, and detergent; ammonia and NaOCl	Chlorine, ammonia	Acute illness with recovery in days.	a
Case report	Ammonia type and hypochlorite cleaners	Ammonia	Acute illness with recovery in days.	b
Case report	Bleach (5.25% NaOCl) and powder containing 80% NaHSO ₄	Chlorine gas	Acute illness with recovery after several days	c
Case report	Several products applied to clear a clogged drain ^b	Uncertain	Severe obstructive airway disease	d
Case reports (2)	NaOCl (5%) and HCl (10%)	Chlorine gas	Acute illness with recovery in several days	e
Case report	Ammonia with household bleach containing hypochlorite	Chloramines	Acute illness with recovery in days.	f
Case reports (3)	Aqueous ammonia (5-10%) with bleach (5.25% NaOCl), plus laundry detergent in 2 cases	Chloramines	Life-threatening toxic pneumonitis requiring prolonged hospitalization and residual symptoms	g
Case reports (5 episodes at 2 state hospitals)	Bleach (NaOCl) and phosphoric acid cleaner	Chlorine	Acute poisoning symptoms that abated within hours to days; a few cases required medical treatment	h
Analysis of 216 cases reported to Regional Poison Information Center	Hypochlorite containing product with (a) ammonia (50%), (b) acid (29%), (c) alkali (21%)	Chlorine/ chloramines	Symptom resolution for 93% of patients within 6 h; 33% received medical care; one patient w/ preexisting condition required hospital admission for continued respiratory distress	i
Case report	Sequential application of numerous cleaning products to remove a bathtub stain ^c	Hydrofluoric acid	Hemorrhagic alveolitis and adult respiratory distress syndrome; month-long hospital care; residual pulmonary deficit	j
Case reports (2 cases each w/ 36 soldiers)	Liquid bleach and ammonia mixed in toilet bowls and buckets	Chloramine gas	Acute symptoms; two patients admitted to hospital, one required several days of intensive care observation	k
Case report	Liquid ammonia (3-10% NH ₃ (aq)) and bleach (5% NaOCl)	Chloramine gas	Upper air compromise and pneumonitis requiring emergency tracheostomy and 7 d of hospital care	l
Case report	Bleach and ammonia	Chloramine gas	Death	m

^a References: a — Faigel, 1964; b — Dunn and Ozere, 1966; c — Jones, 1972; d — Murphy et al., 1976; e — Gapany-Gapanavicius et al., 1982a; f — Gapany-Gapanavicius et al., 1982b; g — Reisz and Gammon, 1986; h — Hattis et al., 1991; i — Mrvos et al., 1993; j — Bennion and Franzblau, 1997; k — Pascuzzi and Storrow, 1998; l — Tanen et al., 1999; m — Cohle et al., 2001.

^b Products used (selected active ingredients): Liquid Plum-R (NaOCl, 5%; KOH, 2%); Drano (NaOH, 54%; NaNO₃, 30%); Clorox (NaOCl, 5%); Sani Flush (NaHSO₄, 75%).

^c Cleaning products used (active ingredient, if reported): cleanser, mildew stain remover (NaOCl, 25-45%), tub and tile cleaner (H₃PO₄, 18%), ammonia cleaner (NaOH, 2-2.5%), bleach (NaOCl, 5.25%), toilet cleaner (HCl, 14.5%), vinegar (CH₃COOH, 5%), rust remover (H₆F₆, 8%). Application of each product was followed by a cold-water rinse.

Table 2.4. Documented associations of asthma, allergy, and sick-building syndrome symptoms in relation to cleaning product use.

Key Finding	Ref ^a
Dried detergent residue from carpet shampoo “caused respiratory irritation among most employees in an office building and among all staff members and most children in a day-care center.”	a
Excessive application of carpet shampoo was associated with widespread, transient, mild respiratory illness among conference attendees	b
Case report of occupational asthma in a cleaning worker caused by inhalation exposure to ethanolamine from a floor-cleaning detergent.	c
Case report of occupational asthma in a pharmacist attributed to indirect exposure to lauryl dimethyl benzyl ammonium chloride from a floor-cleaning product regularly used in his workplace	d
With data from 22 offices in 12 California buildings; researchers found a principal component vector associated with use of cleaning products and air fresheners was useful in predicting stuffy nose (OR = 1.6) and composite irritated mucous membrane symptoms (OR = 1.4).	e
Population-based study of occupational asthma revealed that “cleaners” had the fourth highest odds ratio (1.97) for “bronchial hyperresponsiveness and asthma symptoms or medication.”	f
Prospective study design indicated increased risk of eye, nose, and throat symptoms, asthma and bronchitis associated with “use of sprayers” among current cleaners as compared with former cleaners.	g
Case report of anaphylactic shock with respiratory failure secondary to carpet cleaning in 42-y female; hospitalized for 18 d then released.	h
Case reports of female nurses who exhibited occupational asthma following exposure to surfaces cleaned with solutions containing benzalkonium chloride. Cases were also occupationally exposed to this chemical as a disinfectant.	i
Asthma prevalence for indoor cleaners in Spain was 1.7 times the rate for office workers. Risk mainly associated with cleaning of private homes; “may be explained by the use of sprays and other products in kitchen cleaning and furniture polishing.”	j
Population study of women in Finland revealed a relative risk of asthma of 1.5 for cleaners as compared with those employed in administrative work.	k
Twelve percent of confirmed cases of work-related asthma in California, Michigan, Massachusetts, and New Jersey were associated with exposure to cleaning products	l
“Janitors, housekeepers, and cleaners” was the occupational group with the highest number of reported cases of occupational asthma in Sao Paulo, Brazil, and “cleaning products” was the most commonly reported exposure agent.	m
“Cleaning materials” are the most frequently reported agents for work-related reactive airways dysfunction syndrome cases in Michigan, New Jersey, Massachusetts, and California	n
In NHANES III survey of US workers, occupation of “cleaning” associated with elevated odds ratio of work-related wheezing (OR = 5.4, 95% CI = 2.4-12.2) and work-related asthma, although not statistically significant for latter (OR = 2.4, 95% CI = 0.5-10.6).	o
Population-based incident case-control study of relation between occupation and risk of developing asthma showed an association, but not statistically significant for women cleaners (OR = 1.42, 95% CI = 0.81-2.48)	p
Current or former employment as domestic cleaner was associated with a statistically significant increase in the prevalence of asthma in Barcelona, Spain; symptoms were associated with exposure to bleach and possibly other irritant agents	q
Use frequency of chemical based household products during prenatal period was associated with persistent wheeze in young children. Among eleven products included in analysis were disinfectant, bleach, carpet cleaner, window cleaner, and air fresheners.	r

^a References: a — Kreiss et al., 1982; b — Robinson et al., 1983; c — Savonius et al., 1994; d — Burge and Richardson, 1994; e — Ten Brinke et al., 1998; f — Kogevinas et al., 1999; g — Nielsen and Bach, 1999; h — Lynch, 2000; i — Purohit et al., 2000; j — Zock et al., 2001; k — Karjalainen et al., 2002; l — Rosenman et al., 2003; m — Mendonça et al., 2003; n — Henneberger et al., 2003; o — Arif et al., 2003; p — Jaakkola et al., 2003; q — Medina-Ramón et al., 2003, 2005; r — Sherrieff et al., 2005.

Table 2.5a. Reported volatile constituents of cleaning products listed under California's Proposition 65 or as a Toxic Air Contaminant.

Chemical	CAS No.	Guidelines ^a		Cleaning product (reference)
		NSRL	REL	
Glycol ethers				
Ethylene glycol monobutyl ether (2-butoxy ethanol)	111-76-2	—	+	All purpose cleaner, glass and surface cleaners, lemon fresh and antibacterial spray (Zhu et al., 2001); liquid wax (Knöppel and Schauenberg, 1989)
Diethylene glycol monoethyl ether (2-(2-ethoxyethoxy)ethanol)	111-90-0	—	+	Air freshener (Cooper et al., 1995)
Diethylene glycol monobutyl ether (2-(2-butoxyethoxy) ethanol)	112-34-5	—	+	Hard surface cleaners (Gibson et al., 1991); floor-finish stripper, floor cleaner (Zhu et al., 2001); floor polish (Vejrup, 1996)
Hydrocarbons				
Benzene	71-43-2	7 µg/d	60 µg/m ³	Liquid detergent, steel wool soap pads, furniture wax (Wallace et al., 1987)
Xylenes	1330-20-7	—	700 µg/m ³	Liquid detergent, steel wool soap pads (Wallace et al., 1987); household cleaners & polishes (Sack et al., 1992)
Toluene	108-88-3	7 mg/d ^b	300 µg/m ³	Disinfectant bathroom cleaner (Akland and Whitaker, 2000); lemon fresh and antibacterial spray (Zhu et al., 2001); household cleaners & polishes (Sack et al., 1992); paste wax, detergent, liquid floor waxes (Knöppel and Schauenberg, 1989)
Ethylbenzene	100-41-4	—	2 mg/m ³	Household cleaners & polishes (Sack et al., 1992); paste wax, liquid wax (Knöppel and Schauenberg, 1989); furniture polish (Tichenor and Mason, 1988); steel wool soap pad (Wallace et al., 1987)
Styrene	100-42-5	—	900 µg/m ³	Floor cleaner (Akland and Whitaker, 2000); Liquid wax (Knöppel and Schauenberg, 1989)
n-Hexane	110-54-3	—	7 mg/m ³	Household cleaners & polishes (Sack et al., 1992); paste wax; liquid wax (Knöppel and Schauenberg, 1989)
Carbonyls				
Formaldehyde	50-00-0	40 µg/d	3 µg/m ³	Wood-floor cleaning spray (Akland and Whitaker, 2000); liquid floor detergent (Colombo et al., 1991)
Acetaldehyde	75-07-0	90 µg/d	9 µg/m ³	Detergent/cleanser, liquid wax (Knöppel and Schauenberg, 1989)
Methyl ethyl ketone (2-Butanone)	78-93-3	—	+	Liquid floor waxes (Knöppel and Schauenberg, 1989); specialized cleaner (Salthammer, 1999)

Table 2.5a. (continued) Reported volatile constituents of cleaning products listed under California’s Proposition 65 or as a Toxic Air Contaminant.

<i>Chlorinated organics</i>				
Carbon tetrachloride	56-23-5	5 µg/d	40 µg/m ³	Household cleaners & polishes (Sack et al., 1992)
Dichloromethane (methylene chloride)	75-09-2	200 µg/d	400 µg/m ³	Household cleaners & polishes (Sack et al., 1992)
Tetrachloroethylene (perchloroethylene)	127-18-4	14 µg/d	35 µg/m ³	Household cleaners & polishes (Sack et al., 1992)
1,1,1-Trichloroethane (methyl chloroform)	71-55-6	—	1 mg/m ³	Household cleaners & polishes (Sack et al., 1992); chlorine bleach scouring powder (Wallace et al., 1987)
Trichloroethylene	79-01-6	80 µg/d	600 µg/m ³	Household cleaners & polishes (Sack et al., 1992)
Trichloromethane (chloroform)	67-66-3	40 µg/d	300 µg/m ³	Household cleaners & polishes (Sack et al., 1992); chlorine bleach scouring powder (Wallace et al., 1987)
Propylene dichloride (1,2-dichloropropane)	78-87-5	+	+	Paste wax; liquid floor wax (Knöppel and Schauenberg, 1989)
<i>Other</i>				
1,4-Dioxane	123-91-1	30 µg/d	3 mg/m ³	Household cleaners & polishes (Sack et al., 1992)
Acetophenone	98-86-2	—	+	Liquid waxes (Knöppel and Schauenberg, 1989)

^a NSRL — No significant risk level is the “daily intake level calculated to result in one excess case of cancer in an exposed population of 100,000, assuming lifetime (70-year) exposure at the level in question. REL — Chronic reference exposure levels represent exposure concentrations that would pose no significant health risk to individuals indefinitely exposed to that level. A “+” in either column indicates that the compound is listed as “known to cause cancer” (NSRL) or as a toxic air contaminant (REL), but that the quantitative exposure guideline has not been established. A “—” in either column indicates that the compound has not been listed under the respective program. References for the guideline columns of this table: Proposition 65 chemicals list: http://www.oehha.org/prop65/prop65_list/Newlist.html; Toxic air contaminant list: <http://www.arb.ca.gov/toxics/quickref.htm>; No-significant risk levels: <http://www.oehha.org/prop65/pdf/June2003StatusReport.pdf>; Reference exposure levels: http://www.oehha.org/air/chronic_rels/Allchrels.html.

^b Toluene is listed under Proposition 65 as a reproductive toxicant and the guideline represents the “maximum allowable dose level.”

Table 2.5b. California emissions inventory for organic compounds from selected consumer products that are also listed in the California Toxic Air Contaminant identification program. ^a

			Emissions^b (kg d⁻¹)						
Chemical	CAS No.	TAC ID^c	DIS	GPD	GPC	GLC	FMP	SRM	MPS
<i>Glycol ethers</i>									
2-Butoxyethanol	111-76-2	IIa ^d	41	580	2030	1430		96	17
2-(2-Butoxyethoxy)ethanol	112-34-5	IIa ^d	1.1	0.5	20				
2-(2-Ethoxyethoxy)ethanol	111-90-0	IIa ^d	2.6				0.8	0.7	
2-(2-Methoxyethoxy)ethanol	111-77-3	IIa ^d			2.4				
<i>Hydrocarbons</i>									
Cyclohexane	110-82-7	IVb							8.4
Ethylbenzene	100-41-4	IIa							9.7
<i>n</i> -Hexane	110-54-3	IIa		370					160
Toluene	108-88-3	IIa							640
Xylene isomers	1330-20-7	IIa						5.8	50
<i>Oxygenated organics</i>									
Diethanolamine	111-42-2	IIa	0.5						
1,2-Epoxybutane	106-88-7	IIa							0.7
Isopropyl alcohol	67-63-0	IIb	360	51	1530	1680	2.1	240	88
Methanol	67-56-1	IIa	0.5	16	0.7				330
Methyl ethyl ketone	78-93-3	IIa							420
Methyl isobutyl ketone	108-10-1	IVa							92
<i>sec</i> -Butyl alcohol	78-92-2	IVb							4.3
<i>Chlorinated organics</i>									
Dichloromethane	75-09-2	IIa		8.7				1.7	46
Perchloroethylene	127-18-4	I		73	65			3.7	70
1,1,1-Trichloroethane	71-55-6	IIa						7.2	50
Trichloroethylene	79-01-6	IIa		140				11	150

Table 2.5b. (continued)

^a References: California Air Resources Board Toxic Air Contaminant Identification Program (<http://www.arb.ca.gov/toxics/id/id.htm>; December 1999 list); Emissions inventory (<http://www.arb.ca.gov/ei/speciate/cprodsactgsprof.htm>; February 2003).

^b Total daily mass emissions in California of chemical as tabulated in emissions inventory for seven classes of consumer products: DIS — disinfectants; GPD — general-purpose degreaser; GPC — general-purpose cleaner; GLC — glass cleaner; FMP — furniture maintenance product; SRM — spot removers; and MPS — multi-purpose solvent.

^c ARB's toxic air contaminants identification program assigns each chemical to one of six categories, according to the following criteria (<http://www.arb.ca.gov/toxics/catable.htm>):

Category I: "Substances identified as Toxic Air Contaminants, known to be emitted in California, with a full set of health values reviewed by the Scientific Review Panel."

Category IIa: "Substances identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development by the Office of Environmental Health Hazard Assessment for review by the Scientific Review Panel."

Category IIb: "Substances NOT identified as Toxic Air Contaminants, known to be emitted in California, with one or more health values under development by the Office of Environmental Health Hazard Assessment for review by the Scientific Review Panel."

Category III: "Substances known to be emitted in California and are NOMINATED for development of health values or additional health values."

Category IVa: "Substance identified as Toxic Air Contaminants, known to be emitted in California and are TO BE EVALUATED for entry into Category III."

Category IVb: "Substance NOT identified as Toxic Air Contaminants, known to be emitted in California and are TO BE EVALUATED for entry into Category III."

^d These chemicals belong to the class "glycol ethers." This class is categorized as belonging to Category IIa.

Table 2.6. Sorption studies of target cleaning-product chemicals on indoor surface materials.

Chemical	CAS No.	Indoor material (reference) ^a
<i>Glycol ethers</i>		
Diethylene glycol monobutyl ether	112-34-5	gypsum board (f, g, u), carpet (g, u), stainless steel (f)
Ethylene glycol monobutyl ether	111-76-2	gypsum board (h, p, r, w), carpet (h, p, w), vinyl wallcovering (h, p), wallpaper (p), textile wallcovering (p) acrylic wallcovering (p), PVC flooring (p)
<i>Hydrocarbons</i>		
Benzene	71-43-2	whole homes (e), furnished research room (aa)
Ethylbenzene	100-41-4	carpet (a, v, x, y, z), carpet pad (x, z), vinyl flooring (a, b, y, z), gypsum board (a, v, y, z), ceiling tile (a, v, z), plywood (b), pillow (v), glass (v), wood flooring (y, z), fiberglass shower stall (z), upholstery (z), furnished research room (aa)
Styrene	100-42-5	whole homes (e)
Toluene	108-88-3	carpet backing (b), carpet (d, l, m, n, p, w, x, y, z), carpet pad (x, z), carpet fibers (k), polyester curtains (d), textiles (j, z), cotton sofa (d), cotton curtains (m), whole homes (e), vinyl flooring (i, m, n, p, y, z), gypsum board (p, r, s, w, y, z), wallpaper (p) textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), acrylic paint (s), stainless steel (w), wood flooring (y, z), ceiling tile (z), fiberglass shower stall (z), furnished research room (aa)
Xylene	1330-20-7	whole homes (e), wallpaper (p, q), carpet (p, q, w), acrylic paint on wallpaper (q), PVC (q), aerated concrete (q), gypsum board (p, q, r, w), marble (q), wooden parquet (q), textile wallcovering (p), acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p), furnished research room (aa)
<i>Carbonyls</i>		
Formaldehyde	50-00-0	gypsum wallboard (o)
Methyl ethyl ketone	78-93-3	acrylic paint (s), gypsum board (s), furnished research room (aa)
<i>Chlorinated organics</i>		
Propylene dichloride	78-87-5	whole homes (e)
Tetrachloroethylene	127-18-4	whole homes (e, t), carpet (h, p, t, v, w, x, z), carpet pad (x, z), vinyl wallcovering (h, p), gypsum wallboard (h, p, r, s, v, w, z), wallpaper (p), textile wallcovering (p), acrylic wallcovering (p), PVC flooring (p, z), acrylic paint (s), painted surfaces (t), ceiling tile (v, z), glass (v), pillow (v), wood flooring (z), fiberglass shower stall (z), upholstery (z)
1,1,1-Trichloroethane	71-55-6	whole homes (e), textiles (j), carpet fibers (k)
Trichloroethylene	79-01-6	nylon (c), wool (c), polypropylene (c), jute (c), styrene-butadiene rubber (c), glass (c), polyester (c), cotton (c)
Trichloromethane	67-66-3	whole homes (e)
<i>Alcohols</i>		
Linalool	78-70-6	wallpaper (p), textile wallcovering (p) acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p), gypsum board (p, r), carpet (p)
<i>Terpenes</i>		
Limonene	138-86-3	carpet (w), gypsum board (w), furnished research room (aa)
α -Pinene	80-56-8	carpet (h, l, m, n, p), vinyl wallcovering (h, p), gypsum (h, p, r), PVC flooring (m, n, p), cotton curtains (m), wallpaper (p), textile wallcovering (p) acrylic wallcovering (p), furnished research room (aa)
β -Pinene	127-91-3	wallpaper (p), textile wallcovering (p) acrylic wallcovering (p), vinyl wallcovering (p), PVC flooring (p), gypsum board (p, r), carpet (p)

^a References: a — An et al., 1999; b — Bodalal et al., 2000; c — Borrazzo et al., 1993; d — Bouhamra and Elkilani, 1999a; e — Bouhamra and Elkilani, 1999b; f — Chang et al., 1997; g — Chang et al., 1998; h — Colombo et al., 1993; i — Cox et al., 2001; j — Elkilani et al., 2001; k — Elkilani et al., 2003; l — Jørgensen and Bjørseth, 1999; m — Jørgensen et al., 1999; n — Jørgensen et al., 2000; o — Matthews et al., 1987; p — Meininghaus et al., 1999; q — Meininghaus et al., 2000; r — Meininghaus and Uhde, 2002; s — Popa and Haghighat, 2003; t — Sparks et al., 1991; u — Sparks et al., 1999; v — Tichenor et al., 1991; w — van der Wal et al., 1998; x — Won et al., 2000; y — Won et al., 2001a; z — Won et al., 2001b; aa — Singer et al., 2004.

Table 2.7. Constituents of cleaning product and air fresheners containing C=C bonds.

Chemical	CAS No.	Product (reference)
<i>Alcohols</i>		
Citronellol	106-22-9	Major constituent of rose oil (Kirk-Othmer, 1998)
Dicyclopentadiene alcohol	27137-33-3	Liquid floor detergent (Colombo et al., 1991)
Dihydromyrcenol	18479-58-8	Liquid floor detergent (Colombo et al., 1991); one of the principal components of lavender
Geraniol	624-15-7	Constituent of rose oil and citronella oil (Kirk-Othmer, 1998)
Linalool	78-70-6	Air freshener (Cooper et al., 1995; Salthammer, 1999); liquid floor detergent (Colombo et al., 1991); one of the principal components of bergamot
α -Terpineol ^a	98-55-5	Liquid cleaner/disinfectant, liquid floor detergent (Colombo et al., 1991); air freshener (Salthammer, 1999); cleaning agents (Vejrup and Wolkoff, 1994); major component of pine oil
<i>Aldehydes</i>		
Citronellal	106-23-0	Present in balm mint and citronella oil (Kirk-Othmer, 1998)
Geranial	5392-40-05	Present in lemon grass, rose and orange oil (Kirk-Othmer, 1998)
Neral	106-26-3	Present in rose and orange oil (Kirk-Othmer, 1998)
<i>Aromatic hydrocarbon</i>		
Styrene	100-42-5	Floor cleaner (Akland and Whitaker, 2000); liquid wax (Knöppel and Schauenberg, 1989)
<i>Ether</i>		
3-Butenylpropylether		Detergent/cleaner (Knöppel and Schauenberg, 1989)
<i>Esters</i>		
Linalyl acetate ^a	115-95-7	Air freshener (Salthammer, 1999); one of the principal components of bergamot
Methyl methacrylate ^b	80-62-6	Cleaning agents (Wolkoff et al., 1998)
<i>Terpenes</i>		
Camphene	79-92-5	Liquid cleaner/disinfectant (Colombo et al., 1991); antibacterial glass and surface cleaner, all-purpose cleaner (Zhu et al., 2001); cleaning agents (Vejrup and Wolkoff, 1994); air freshener (Cooper et al., 1995)
3-Carene	13466-78-9	Liquid cleaner/disinfectant, floor wax (Colombo et al., 1991); antibacterial glass and surface cleaner (Zhu et al., 2001)
Limonene	138-86-3	Floor wax (Colombo et al., 1991); room freshener (Tichenor & Mason, 1988); detergent/cleaner (Knöppel & Schauenberg, 1989; Maroni et al., 1995); air freshener (Cooper et al., 1995; Salthammer, 1999); cleaning agents (Vejrup & Wolkoff, 1994); all-purpose cleaner, glass and surface cleaner, antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001)

Table 2.7. (continued) Constituents of cleaning product and air fresheners containing C=C bonds.

β -Myrcene	123-35-3	All-purpose cleaner, antibacterial glass and surface cleaner (Zhu et al., 2001); air freshener (Cooper et al., 1995; Salthammer, 1999)
Ocimene	13877-91-3	Air freshener (Zhu et al., 2001; Salthammer, 1999)
α -Phellandrene	99-83-2	Antibacterial glass and surface cleaner (Zhu et al., 2001)
α -Pinene	80-56-8	Liquid cleaner/disinfectant, floor wax (Colombo et al., 1991); antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001); air freshener (Salthammer, 1999)
β -Pinene	127-91-3	Floor wax, liquid cleaner/disinfectant (Colombo et al., 1991); all-purpose cleaner, antibacterial glass and surface cleaner, lemon fresh and antibacterial spray, floor shine cleaner (Zhu et al., 2001)
α -Terpinolene	586-62-9	Cleaning agents (Vejrup and Wolkoff, 1994)
α -Terpinene	99-86-5	Major constituent of pine oil (Kirk-Othmer, 1998)
<i>Sesquiterpenes</i>		
Caryophyllene	87-44-5	Wood polishes and waxes (Kirk-Othmer, 1998)
α -Humulene	6753-98-6	Wood polishes and waxes (Kirk-Othmer, 1998)
Longifolene	475-20-7	Wood polishes and waxes; scenting agent (Kirk-Othmer, 1998; Gosselin et al., 1984)
α -Cedrene	469-61-4	Wood polishes and waxes; scenting agent (Kirk-Othmer, 1998; Gosselin et al., 1984)
<i>Fatty Acids</i>		
Oleic acid	112-80-1	Wood polishes and waxes (Kirk-Othmer, 1998)
Linoleic acid	60-33-3	Major constituent of linseed oil (Kirk-Othmer, 1998)
Linolenic acid	463-40-1	Major constituent of linseed oil (Kirk-Othmer, 1998)

^a Compound produced in relatively large amounts, but little published information on reactions with ozone, hydroxyl radicals or nitrate radicals.

^b Residual monomers from polymers.

Table 2.8. Reported 2nd order rate constants, k , and calculated pseudo 1st order rate constants, k' , for the reactions of selected unsaturated constituents of cleaning products and air fresheners with ozone, hydroxyl radicals and nitrate radicals. ^a

Compound	Reaction with O ₃ ^a			Reaction with OH ^a			Reaction with NO ₃ ^a		
	k (ppb ⁻¹ s ⁻¹)	R ^b	k' (h ⁻¹)	k (ppb ⁻¹ s ⁻¹)	R ^b	k' (h ⁻¹)	k (ppb ⁻¹ s ⁻¹)	R ^b	k' (h ⁻¹)
camphene	2.2×10^{-8}	d	0.002	1.3	d	0.024	0.016	a	0.06
longifolene	$<1.7 \times 10^{-7}$	l	0.01	1.2	m	0.021	0.017	m	0.06
beta-pinene	3.7×10^{-7}	e	0.03	2.0	b	0.035	0.06	a	0.22
styrene	4.2×10^{-7}	n	0.03	1.4	c	0.026	0.004	a	0.01
alpha-cedrene	6.9×10^{-7}	l	0.05	1.6	m	0.030	0.20	m	0.73
geraniol	7.5×10^{-7}	p	0.05	na			na		
delta-3-carene	9.3×10^{-7}	e	0.07	2.1	b	0.038	0.22	a	0.81
β-phellandrene	1.2×10^{-6}	k	0.08	4.1	k	0.074	0.20	k	0.71
cyclohexene	1.8×10^{-6}	h	0.13	1.3	j	0.024	0.013	a	0.05
geranylacetone	1.9×10^{-6}	q	0.13	na			na		
alpha-pinene	2.1×10^{-6}	e	0.15	1.3	b	0.024	0.15	a	0.55
sabinene	2.2×10^{-6}	e	0.16	2.9	d	0.052	0.25	a	0.89
γ-terpinene	3.4×10^{-6}	e	0.25	3.2	i	0.058	0.72	a	2.6
copaene	3.9×10^{-6}	l	0.28	2.2	m	0.040	0.39	m	1.4
d-limonene	5.2×10^{-6}	e	0.37	4.2	b	0.075	0.30	a	1.1
2-carene	5.9×10^{-6}	e	0.42	2.0	g	0.035	0.46	a	1.7
longipinene	7.1×10^{-6}	q	0.51	na			na		
α-terpineol	7.4×10^{-6}	o	0.53	4.7	O	0.084	na		
linalool	1.1×10^{-5}	f	0.76	3.9	f	0.070	0.28	f	1.0
myrcene	1.2×10^{-5}	e	0.86	5.2	b	0.094	0.26	a	0.94
ocimene	1.4×10^{-5}	e	0.99	6.2	b	0.11	0.55	a	2.0
terpinolene	4.7×10^{-5}	l	3.4	5.5	g	0.10	2.4	a	8.6
α-phellandrene	7.4×10^{-5}	l	5.3	7.6	b	0.14	2.1	a	7.6
γ-cadinene	7.9×10^{-5}	q	5.7	na			na		
aromadendrene	1.6×10^{-4}	q	12	na			na		
caryophyllene	3.0×10^{-4}	l	21	4.9	m	0.089	0.47	m	1.7
humulene	2.9×10^{-4}	l	21	7.1	m	0.13	0.86	m	3.1
α-terpinene	5.2×10^{-4}	l	37	8.9	b	0.16	4.5	a	16
trans-nerolidol	5.7×10^{-4}	q	41	na			na		
cis-nerolidol	7.6×10^{-4}	q	55	na			na		

^a See text for references supporting the assumed levels of O₃, OH and NO₃ used to calculate k' : [O₃] at 20 ppb, [OH] at 5×10^{-6} ppb, [NO₃] at 1×10^{-3} ppb.

^b References: a — Atkinson, 1991; b — Atkinson et al., 1986; c — Atkinson and Aschmann, 1988; d — Atkinson et al., 1990a; e — Atkinson et al., 1990b; f — Atkinson et al., 1995; g — Corchnoy and Atkinson, 1990; h — Greene and Atkinson, 1992; i — Grosjean and Williams, 1992; j — Rogers, 1989; k — Shorees et al., 1991; l — Shu and Atkinson, 1994; m — Shu and Atkinson, 1995; n — Tuazon et al., 1993; o — Wells, 2005; p — Nunes et al., 2005; q — Pollman et al., 2005.

Table 2.9. Products (reported or inferred for indoor settings) derived from reactions between unsaturated organic compounds and ozone, hydroxyl radicals or nitrate radicals.

Product	Product of Reaction with			Refs ^a
	O ₃	OH	NO ₃	
Primary ozonides	✓			a, d
Stabilized Crigee biradicals (carbonyl oxides)	✓			d, p, q
Hydroxyl radical	✓			l, o t, u
Alkyl radicals		✓	✓	a, d
Hydroxyalkyl radicals		✓		a
Nitrooxyalkyl radicals			✓	a
Hydroperoxy radical	✓	✓	✓	l, n, v
Alkoxy radicals	✓	✓	✓	a, d, n
Unidentified radical	✓			b
α-Hydroxyhydroperoxides	✓	✓		a, c
Hydrogen Peroxide	✓			h, i
Hydroperoxides	✓			a, h, i, p, q
Peroxy-hemiacetals	✓			p, q
Secondary ozonides	✓			k, p, q
Epoxides	✓			a
Hydroxy carbonyls		✓		a
Dihydroxy carbonyls		✓		a
Hydroxy nitrates			✓	a
Carbonyl nitrates			✓	a
Formaldehyde	✓	✓		a, d
Other aldehydes (saturated and unsaturated)	✓	✓	✓	a, d, y
Acetone	✓	✓		a, d
Other ketones (saturated and unsaturated)	✓	✓	✓	a, d, y
Formic acid	✓	✓		a
Other carboxylic acids	✓	✓		a
Organic nitrates		✓	✓	a
Multifunctional oxidation products with carbonyl, carboxylate and/or hydroxyl groups	✓	✓	✓	d, e, f, r, x
Secondary organic aerosols via gas/particle partitioning of low volatility products	✓	✓	✓	i, l, s, v, w

^a References: a — Atkinson and Arey, 2003; b — Clausen and Wolkoff, 1997; c — Fick et al., 2003; d — Finlayson-Pitts and Pitts, 2000; e — Glasius et al., 2000; f — Griffin et al., 1999; g — Jang and Kamens, 1999; h — Li, 2001; i — Li et al., 2002; j — Long et al., 2000; k — Morrison, 1999; l — Nazaroff and Cass, 1986; m — Rohr et al., 2003; n — Sarwar et al., 2002a; o — Sarwar et al., 2002b; p — Tobias and Ziemann, 2000; q — Tobias et al., 2000; r — Virkkula et al., 1999; s — Wainman et al., 2000; t — Weschler and Shields, 1996; u — Weschler and Shields, 1997a; v — Weschler and Shields, 1997b; w — Weschler and Shields, 1999; x — Yu et al., 1998; y — Shu et al., 1997.

Table 2.10. Summary of findings from literature review.

-
- **Importance of high intake fraction for indoor sources.** Because the intake fraction for indoor releases may be 100 to 1000 times higher than the intake fraction for outdoor releases, inhalation intake of the 32 tonnes per day of volatile organic compounds emitted from cleaning product use in California may be comparable to the inhalation intake of the 2400 tonnes per day of volatile organic compounds released to ambient air from all sources in the state.
 - **Accidental poisonings.** Over almost four decades (1964-2001), thirteen articles appeared in the archival, peer-reviewed literature that documented adverse health consequences from inhaling fumes from inappropriately mixed cleaning products. Many of these incidents involved combining bleach and ammonia.
 - **Asthma, allergy, and sick-building syndrome (SBS) symptoms.** During the past quarter century (1982-2005), eighteen papers have been published that document associations between use of cleaning products, or cleaning as an occupation, and asthma, allergic, or SBS symptom responses. Especially noteworthy are many recent studies showing an association between occupational asthma and employment as a domestic cleaner or janitor.
 - **Presence of toxic air contaminants (TACs) in cleaning products.** Using measurements published in the archival literature from anywhere in the world, 21 chemicals were identified that have been found in cleaning products and also appear on California's list of TACs. A California-specific emissions inventory using 1997 data, which were self-reported by manufacturers, identified 16 chemicals have been identified as California TACs (Category I or IIa) and are emitted from one or more of these consumer product classes: disinfectants, general-purpose degreasers, general-purpose cleaners, glass cleaners, furniture maintenance products, spot removers, and multi-purpose solvents. Eleven of the chemicals are common to the two lists.
 - **Sorption of TACs on indoor surfaces.** Sorptive interactions between volatile organic chemicals and indoor surfaces can influence the time-pattern of concentrations and, therefore, exposures. More than 30 studies were identified that report on sorptive interactions between certain chemicals found in cleaning products and materials used indoors.
 - **Terpenes and related compounds.** Many cleaning products and air fresheners contain terpenes and related chemicals, which are derived from plant oils. Their use may be as an active ingredient (solvent) or because of their pleasant fragrance. A key characteristic of these compounds is that they contain unsaturated C=C bonds. Many react rapidly with ozone, because this oxidant is effective at attacking C=C bonds.
 - **Secondary pollutants.** Cleaning product constituents, especially terpenes and related compounds, can react rapidly not only with ozone, but also with the hydroxyl radical (OH) and with the nitrate radical (NO₃), all of which may be present in indoor air. The chemistry can generate a host of secondary pollutants, some of which are stable and can be measured (such as formaldehyde), and some of which are short-lived or otherwise pose analytical challenges. This latter group, known as "stealth chemicals," might conceivably contribute to adverse health consequences.
 - **Surface reactions.** Important reactions involving cleaning product or air freshener constituents might occur not only in the gas phase, but also on indoor surfaces.
-

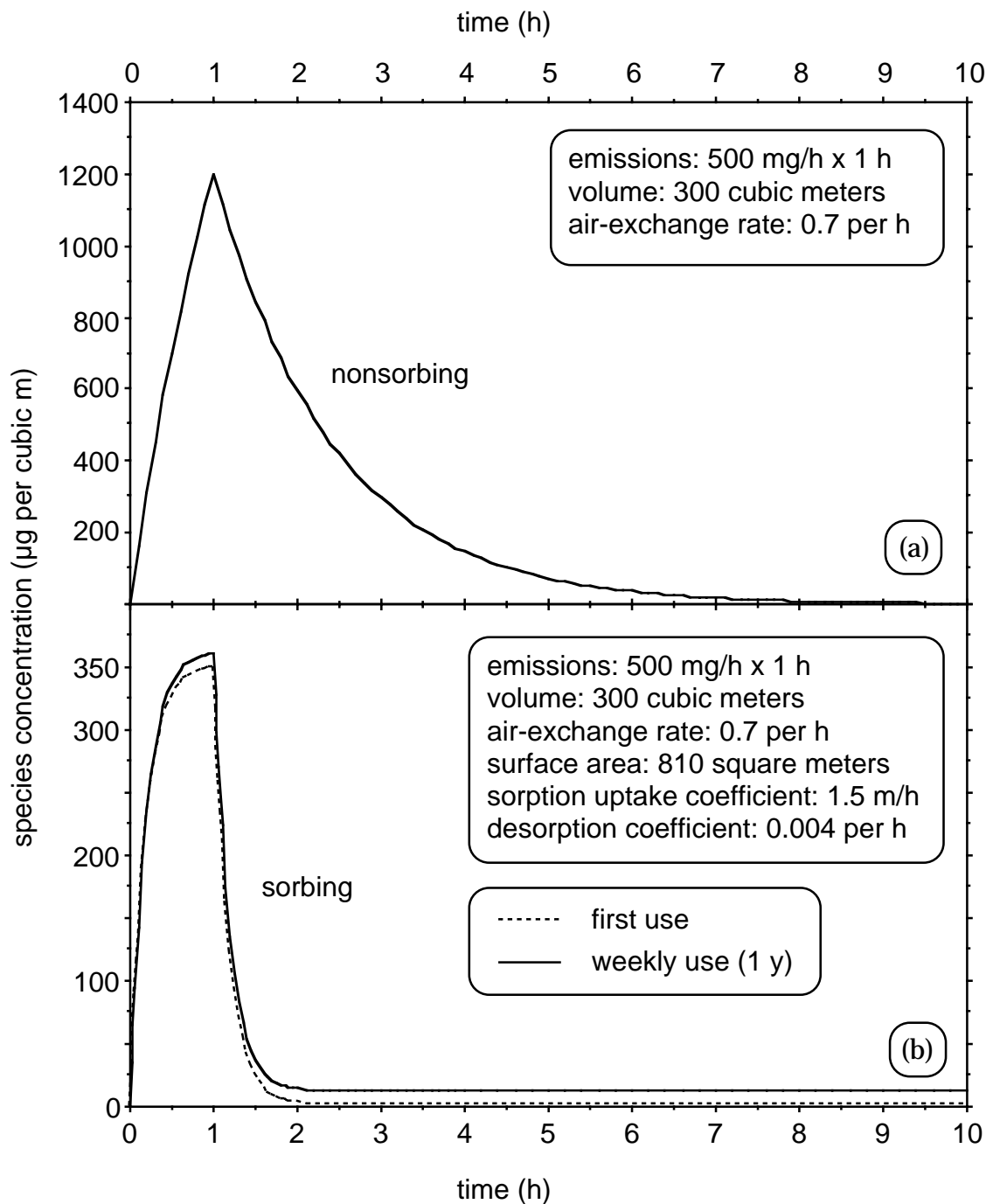


Figure 2.1. Hypothetical concentration of an air contaminant resulting from the primary emissions of a volatile constituent of a cleaning product, used in a single-family home. (a) Nonsorbing contaminant. (b) Sorbing contaminant where sorption model follows work of Tichenor et al. (1991), with $k_a = 1.5 \text{ m h}^{-1}$ and $k_d = 0.004 \text{ h}^{-1}$, based on the findings of Sparks et al. (1999) for 2-(2-butoxyethoxy)butanol on carpet and gypsum board. The “first use” case assumes no sorbed mass at time $t = 0$. The “weekly use (1 y)” case presents simulated results for the last of 52 successive weekly applications.

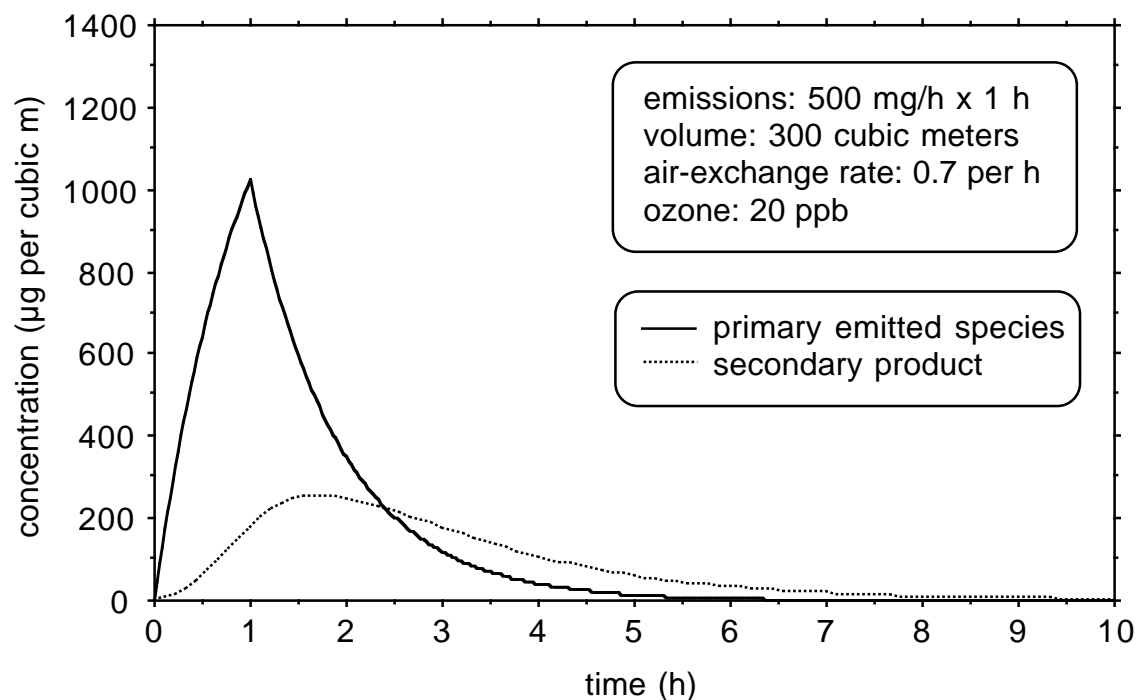


Figure 2.2. Hypothetical concentrations of air contaminants resulting from the primary emissions of a reactive volatile constituent of a cleaning product, used in a single-family home. Basic conditions are the same as in Figure 2.1. The indoor ozone level is assumed constant at 20 ppb. The second-order rate constant is $k = 5.2 \times 10^{-6} \text{ ppb}^{-1} \text{ s}^{-1}$, similar to that for the ozone/limonene reaction (Table 2.8). The concentration of a hypothetical secondary reaction generated by one-to-one stoichiometry is also shown. Both the reacting contaminant and hypothetical product are assumed to be nonsorbing.

3. COMPOSITION AND PRIMARY EMISSIONS FROM CLEANING PRODUCTS AND AIR FRESHENERS

3.1. Introduction

The overall objective of the work reported in this section was to measure the composition and primary emissions of volatile organic compounds (VOCs) for a set of common cleaning products and air fresheners. In the composition measurements, a broad spectrum of VOCs were identified and measured. We focused on regulated toxic constituents, which were mostly ethylene-based glycol ethers, and on terpenes and other unsaturated compounds potentially reactive with ozone. Ethylene-based glycol ethers are of interest because compounds in this class are widely used as solvents in cleaning products and because the class is listed by the USEPA as hazardous air pollutants and by the State of California as toxic air contaminants (TACs). Terpenes and related compounds are widely used in both cleaning products and air fresheners because of their favorable solvent properties and their pleasant scents. Species in this class are known to react rapidly with ozone, and those reactions can produce secondary pollutants of concern, including formaldehyde (a TAC), the hydroxyl (OH) radical, and organic particulate matter. Secondary pollutant formation initiated by reactions with ozone is also of potential concern when other, non-terpene based unsaturated compounds are present in cleaning products or air fresheners.

A shelf survey was conducted to establish a list of products that are readily available to California consumers. From these, fifty products were selected for screening. Using information on the product label and on material data safety sheets, a subset of twenty-one products suspected of containing TACs or terpenes and other unsaturated compounds was selected for characterization of their VOC content. Experiments were conducted to measure the composition of these products. Based on these data and in consultation with the ARB, six products were selected for further study. A series of experiments was conducted in which these products were applied in simulated use in a room-sized research chamber. Time-dependent concentrations and effective emission factors were determined for target analytes. This section of the report describes these activities. Investigations of the reactive chemistry of cleaning-product and air freshener constituents with ozone are described in §4.

3.2 Shelf Survey

3.2.1. Objectives

The primary objective of the product shelf survey was to identify the aerosol, liquid and gel cleaning products and air fresheners that are widely available for sale to California consumers. The secondary objectives were to classify the available cleaning products and air fresheners by type using ARB consumer product category definitions and to identify a subset of widely available products in a number of categories potentially containing TACs such as ethylene-based glycol ethers, terpenoid compounds and possibly other ozone-reactive compounds.

3.2.2. Methods

The product shelf survey was conducted as a multistep process. First, we decided to focus the survey on large chain-store retailers with substantial market presence in California's most populated cities. In addition, we wanted to include a variety of retail store types — such as grocery stores, drug stores, department stores, and hardware/home improvement stores — that are frequented by large numbers of California consumers. Ten chain store retailers broadly

representative of these retailer types were selected. The 15 California cities with the largest populations in year 2000 were identified from a list of the 100 most heavily populated cities in the US, as published online by City Data (<http://www.city-data.com/top1.html>). The total population represented by these 15 cities was 10.4 million. Next, using an online “Yellow Pages” directory (<http://yp.yahoo.com/>), we identified and counted the numbers of outlets for each retailer in each of the 15 cities. In many cases, numbers were checked using “Store Locator” functions on the retailers’ websites.

Using the summary data on the numbers of outlets for the ten chain store retailers, we selected — in consultation with the ARB — five retailers from the original ten for inclusion in the product shelf survey. Working under an assumption that the retailers’ products available for sale are likely to be similar throughout the state, we selected one large store in the East Bay of the San Francisco Bay Area for each of the five retailers. A single surveyor visited each of these stores in August 2002. The surveyor recorded the brand name and the product manufacturer of all aerosol, liquid and gel cleaning products and air fresheners in seven general categories that were physically present on the shelves at the times of the visits. The seven categories included: (1) general-purpose degreasers; (2) general-purpose cleaners; (3) glass and surface cleaners; (4) anti-bacterial sprays and deodorizers; (5) floor cleaners; (6) furniture cleaners and polishes; and (7) air fresheners. All products were recorded irrespective of listed or suspected ingredients. Lower-volume specialty products were included as well as broadly recognized name-brand products. The surveyor also attempted to identify all of the available varieties of a single product. One example of this type of product is an air freshener sold under a single brand or trade name but available in different fragrances. The recorded information for each product included the brand, the product description, the manufacturer, and the product form. Product forms included aerosol spray, concentrated liquid, gel, liquid, and trigger spray. Subsequent to the physical survey, the product descriptions and the manufacturer identifications were checked to the extent possible by referring to manufacturer and distributor or retailer websites. Company mergers or buyouts complicated the identification of manufacturers for some products.

In 2005, with ARB staff assistance, the products were reclassified into 16 official categories defined in a California regulation for reducing volatile organic compound emissions from consumer products (CARB, 2005a).

The next step was to identify a subset of widely available products that might contain the target compounds of interest to the study consisting of ethylene-based glycol ethers such as 2-butoxyethanol (also known as ethylene glycol monobutyl ether or butyl cellosolve, CAS 111-76-2); other TACs such as aromatic hydrocarbon and chlorinated solvents, terpenoids such as d-limonene ((+)-(4R)-limonene, CAS 5989-27-5) and pine oil (CAS 8009-09-3), a mixture that contains several terpenes and terpene alcohols; and other ozone reactive compounds. The primary information used to guide this selection was obtained from Material Safety Data Sheets (MSDSs). The sources of MSDSs included manufacturers’ websites, and the Household Products Database (NIH, 2004) (<http://householdproducts.nlm.nih.gov/>, National Institutes of Health), which provides MSDSs and lists ingredients for many common products. MSDSs also were sought on the University of California’s ChemQuik online database available to UC campuses and to the national laboratories that are operated by the University of California. Information printed on product labels served as another source of information. In a few cases, manufacturers listed ingredients on the labels; but in all of these cases, MSDSs were also available. In some cases, the presence of terpenoids was inferred from the product labels (e.g., lemon scented, lemon fresh, etc.). All of the air fresheners were assumed to contain fragrance

compounds, many of which are presumed to be terpenoids or are unsaturated molecules potentially reactive with ozone.

This process resulted in the identification of 50 products of potential interest to this study. Since the focus of this study is on industry-wide trends in product formulation, all products at this and subsequent stages of the study are identified by code only (i.e., product names and manufacturers are not reported). The employed coding system is based on the 16 ARB product categories with a distinct three character alphabetical code assigned to each category. Within each category, a product is assigned a unique number. For example, AFR-1 identifies air freshener number one.

Through extensive consultation with the ARB, the initial list of 50 products was further reduced to a list of 21 products to be screened by means of chemical measurements for their potential to emit compounds of interest to the study. Here we focused on widely available products most likely to contain and emit the chemicals of interest and to be representative of a range of product categories. Information related to the selection of the 21 products is presented in §3.3.2.

3.2.3. Results

The ten chain store retailers selected for inclusion in the product shelf survey are Safeway/Vons, Albertsons, Longs Drugs, Smart&Final, Wal-Mart, Target, Costco, Home Depot, ACE Hardware, and OSH. Safeway/Vons and Albertsons are large grocery store chains. Smart&Final outlets are warehouse stores offering food and food-service supplies including janitorial and cleaning products. Longs Drugs is a pharmaceutical, drug and variety store chain. Wal-Mart and Costco are chains of large warehouse stores selling a broad range of consumer goods. The Target chain of large stores focuses mostly on household items. The ACE Hardware and OSH (Orchard Supply Hardware) chains focus mainly on hardware and home care items. Home Depot is a chain of warehouse stores serving the home improvement and construction markets.

The numbers of outlets of the ten selected retailers in each of the 15 largest California cities are presented in Table 3.1. A total of 602 retail outlets are indicated. Not surprisingly, the grocery stores are present in most of the 15 cities and together comprise 43 percent of the total number of retail outlets recorded. Wal-Mart and Costco have fewer outlets, but these are large superstores attracting consumers from broad regions.

Five retailers with a presence in the San Francisco Bay area were selected from the list of ten for the product shelf survey. These are Safeway, Longs Drugs, Smart&Final, Wal-Mart and Home Depot. The locations of the five stores that were surveyed are listed in Table 3.2. All are located in the East Bay area.

Products in the seven original general product categories were reclassified into 16 ARB defined consumer product categories. The 16 product categories and the corresponding abbreviations used for the product coding system are listed in Table 3.3. The results of the product shelf survey in which the individual products are identified are presented by category in Appendix A (Tables A.1-A.9). Within each appendix table, the products are alphabetically ordered, first by manufacturer and then by product description. The occurrence of the products on shelves at the five retail chains is indicated in these tables.

The numbers of products by category at each store surveyed are shown in Table 3.4. A total of 291 products are included in the survey. Of these, 25 percent are general-purpose cleaners and 30 percent are air fresheners. Safeway, Smart&Final and Wal-Mart carried the

largest numbers of products. Consistent with its emphasis on janitorial supplies, Smart&Final offered for sale relatively large percentages of general-purpose degreasers plus multi-purpose solvents, floor polishes/waxes plus floor wax strippers, and bathroom-and-tile cleaners plus metal polish/cleaners plus oven cleaners, relative to the other retailers. The numbers of represented manufacturers in each product category also are shown in the table. Relatively large numbers of manufacturers produce general-purpose cleaners and air fresheners.

In Table 3.5, the numbers of products by category are listed for the 18 manufacturers with three or more products in the survey. The two companies with the largest numbers of total products are Reckitt Benckiser and SC Johnson. SC Johnson dominates the air freshener market in terms of the numbers of products offered in this category. The other companies with relatively large numbers of products considering all categories are Acuity Specialty Products Group, Smart & Final, Inc. and The Clorox Company.

Fifty products were selected from the total number of products in the survey as possibly containing and emitting the compounds of interest to this study. Summary information for these candidate products is provided in Table 3.6. Seven product categories are represented. These are disinfectants, general-purpose degreasers, general-purpose cleaners, glass cleaners, wood cleaners, carpet and upholstery cleaners, and air fresheners. Sixteen different manufacturers are represented. For 24 products, the selection was based on information obtained either from MSDSs or from product labels indicating the known or likely presence of the compounds of interest. Each of the eleven air fresheners was assumed to contain compounds of interest. The remaining fifteen products were selected from among well-known brands to provide diversity with respect to the numbers of product categories and products within categories.

3.3. Composition Screening Experiments

3.3.1. Objectives

From the 50 candidate products (as summarized in Table 3.6) and in consultation with ARB staff, we selected 21 widely available cleaning products and air fresheners to be screened for their emissions of VOCs with emphasis on those compounds of particular interest to the study. These products were then subjected to testing. The broad objective was to obtain information on vapor-phase compositions likely to result from the use of these products with focus on ethylene-based glycol ethers, other TACs, unsaturated terpenoid compounds, and other unsaturated compounds potentially reactive with ozone. A gas sampling bag method was developed and utilized for this purpose. In this method, small quantities of the products were volatilized and then sampled for chemical analysis. A further objective was to select a subset of products in each of several categories for subsequent detailed studies of potential inhalation exposures during product use and for additional experiments characterizing reactions of the products' volatile constituents with ozone. To this end, a simple model was used to estimate potential emissions of VOCs for single uses of the products in residences.

3.3.2. Methods

Product selection and collection of product specimens

The initial list of 50 candidate products was reduced to 21 products representative of a range of cleaning products and air fresheners from a variety of manufacturers that were expected to contain and emit VOCs of interest to the study. As explained in §3.2, the names of the selected products have been suppressed and the products are identified in this report using an alphanumeric coding system. The consumer product category information (Table 3.3) is retained

since the category is a main determinant of product application and frequency of use. The 21 products are listed by category in Table 3.7. Also shown are the product forms, which for cleaning products are aerosol spray, liquid, and trigger spray. Seven general-purpose cleaners were selected, as this is the predominant cleaning-product category in terms of the numbers of available products. There were four furniture maintenance products and four air fresheners consisting of three plug-in vaporizers and one aerosol spray. Disinfectants, general-purpose degreasers, glass cleaners, wood cleaners, spot removers, and multi-purpose solvents were each represented by a single product.

Table 3.7 also lists other tables in this report in which quantitative chemical composition data are presented for each of these products. The most extensive measurements were made on seven products that were selected for potential use in subsequent experiments. Six of these products were chosen for simulated-use experiments in which concentrations and emissions of primary constituents were determined. These products are indicated with a checkmark under the “P” column of Table 3.7: GPC-1, GPC-2, GPC-3, GPC-4, GLC-1, and AFR-1. Eighteen experimental runs in a room-sized (50-m³) chamber, labeled 1A-1R, are described in §3.4 of the report. Two of the “P” products, plus one additional product were selected for studies of secondary pollutant formation owing to the interaction of primary constituents with ozone. These products are indicated with a checkmark under the “S” column of Table 3.7: GPD-1, GPC-1, and AFR-1. The experiments are described in §4 of the report. Fifteen experimental runs, labeled 2A-2O, were conducted under steady-flow conditions in a bench-scale (198-L) chamber. An additional eleven experimental runs, labeled 3A-3K, were carried out by simulated use in the room-sized chamber, with or without the simultaneous, deliberate introduction of ozone.

Between September 2002 and January 2003 specimens of 20 products were purchased locally, often from the same retail stores that were the subject of the product shelf survey (Table 3.2). One product, general-purpose cleaner GPC-2, was purchased and evaluated in October 2003. Containers of general-purpose cleaner GPC-1 and glass cleaner GLC-1 with different lot numbers were each purchased from three different retail stores. The specimens were logged noting the date and location of purchase, distinguishing product information, container size, and container lot number. The containers were labeled with the date and location of purchase. Product labels were copied. Product containers were stored in the laboratory in an unopened condition prior to the screening measurements.

Development of experimental protocols

We first developed and tested experimental protocols to screen the selected products for their VOC composition. Our guiding objective in designing these protocols was to efficiently simulate volatilization of the products similar to that which occurs when the products are used as directed. To this end, we focused on methods of volatilizing the products into known volumes of nitrogen gas. A key challenge in developing the protocols was the identification of inexpensive and/or reusable containers that would allow for multiple products to be screened in parallel in the laboratory.

Three different types of containers were evaluated: 2-L glass dilution bulbs, 5-10 L Tedlar® gas sampling bags, and an 80-L stainless steel drum. Experiments were conducted with a general purpose cleaner known to contain terpenoid compounds spanning a range of vapor pressures. Measurements from all three containers produced qualitatively similar information about product composition. Generally, the relative abundances of the product’s least volatile

components were lower in the laboratory test containers compared to the results of a direct analysis of the product diluted in methanol. These discrepancies may have been due to incomplete initial volatilization or by sorption of the less volatile compounds to interior surfaces of the containers.

The reusable 2-L glass dilution bulbs were rejected for further use because cleaning the bulbs to obtain low-background measurements between uses proved difficult, requiring solvent rinsing and considerable labor. The use of the large drum was deemed impractical owing to the need to maintain multiple drums in a temperature-controlled environment and our lack of a facility to wash the drums. Thus, we settled on the most pragmatic solution, using new Tedlar bags to be discarded after each use. We also decided that larger Tedlar bags were needed specifically for products in aerosol form owing to our limited ability to control product spray and the need to determine the amount of product introduced into a bag by weighing the product container before and after use. The protocol development experiments also explored the benefit of heating the Tedlar bag to promote volatilization.

Preparation of product gas samples

Product gas samples were prepared by a procedure we term the “bag method.” Tedlar gas-sampling bags with single polypropylene septum fittings and rated capacities of 5-L and 80-L were purchased (Part Nos. 232-05 and 231-30 respectively; SKC, Inc.). The 5-L bags (30.4 × 31.7 cm) were used for the 15 liquid products. The 80-L bags (71.7 × 77.4 cm) were used for the five aerosol products and the air-freshener gel. Prior to use, each bag was twice filled with high purity nitrogen (99.999%) and evacuated. Bags then were filled with approximately 3-L or 50-L high-purity nitrogen supplied through a mass flow controller calibrated at 298 K and 101.3 kPa. Small bags were filled at 110-120 mL min⁻¹ for 25-27 min. Large bags were filled at 4 L min⁻¹ for approximately 12.5 min. Gas flow rates were checked with a gas-flow meter (Model DryCal® DC-Lite, Bios International). Gas flow rates and filling times were recorded for each sample bag and used to calculate the gas volumes.

Products in liquid form were introduced into the 5-L sample bags using a micro-syringe that was precleaned with methanol. Whenever possible, liquid was drawn directly from the product container; otherwise an aliquot of the product was first dispensed to a precleaned 5-10 mL glass beaker using a new (i.e., used only once and then discarded) glass Pasteur pipette. The syringe was flushed with the product several times by drawing liquid from the bulk product then expunging to a waste container. The desired amount of product then was drawn into the syringe, measured, and injected into the N₂-filled sample bag through the septum port. The volume of product injected was 5 µL for liquid products and 2 µL for the two oily liquid air fresheners.

For an aerosol product, the original spray nozzle was removed and a stainless steel luer-lock syringe needle (No. 20) was fitted to the outlet tube of the can to facilitate injection of the product into the 80-L sample bags. The desired amount of an aerosol product was estimated based on preliminary composition data. An aerosol can with the needle attached was thoroughly shaken immediately before injection. The needle was inserted through the bag septum and the needle was depressed for one to several seconds as estimated to be necessary. The amount of product injected into the bag was determined by weighing the can, with needle attached, before and after the injection on one of two laboratory balances. Product containers less than 360 g were weighed to a resolution of 0.01 g (Model PE360, Mettler). More massive containers were weighed to a resolution of 0.1 g (Model PJ4000, Mettler).

The product contained in plug-in air freshener AFR-3 is a gel; therefore, it could not be introduced into a sample bag by syringe. Instead, a small aliquot of the product was transferred from the plastic packet within the plug-in device onto a strip of aluminum foil that had been pre-cleaned with methanol, dried and pre-weighed. The mass of product was determined by weighing the aluminum strip with the product to a resolution of 0.0001 g (Model AE240, Mettler). Two sample bags were prepared with different product masses. The aluminum foil strip was inserted through a 5 to 10-cm slit that was cut into an empty 80-L Tedlar bag just prior to this procedure. The bag was immediately resealed with 15-cm wide aluminum tape placed over the slit. The bag then was filled with ~50 L nitrogen as described above.

Following product injection, sampling bags were placed into an oven to promote product volatilization. Five-liter bags containing liquid samples were heated to 67-71°C (Model 1330G, VWR Scientific Products). Because of their size, 80-L bags were heated to 39-41°C in a large incubator (Model 1840IR, VWR Scientific Products). After 1 h, 5-L bags were removed from the oven and placed on the laboratory bench at room temperature (approximately 22 to 24°C) where they remained for 1 hr. The large bags were heated for several hours before equilibrating at room temperature.

Collection of gas samples from bags

Gas samples were withdrawn from room temperature equilibrated bags using appropriately sized gas-tight syringes (Pressure-Lok® Series A-2, Vici). These syringes were cleaned between product samples by flushing methanol through the barrel three times and then drying the disassembled parts in an oven. The syringe needle was inserted through the septum port on the bag and a measured gas volume was drawn into the syringe. The syringe valve was closed and the needle was withdrawn from the bag. The gas sample was transferred immediately to a sorbent-based gas sampling tube (described below) through a loading rig. The loading rig consisted of an inlet port with a Teflon-lined septum on a stainless steel tee connector with the sampling tube attached to the straight outlet of the tee and a stream of ultra-pure helium (He, 99.999%) flowing through the branched port of the tee at 100 mL min⁻¹. A separate, dedicated 5-mL gas-tight syringe then was used to introduce an internal gas standard of approximately 100 ng of 1-bromo-4-fluorobenzene (BFB) onto the sampling tube. Helium flow continued through the sampling tube for 5 min following internal standard injection. Sampling tubes immediately were sealed with airtight caps fit with Teflon ferrules and either analyzed the same day or stored in the freezer (< -10°C) until analysis.

Commercially available gas sampling tubes were used (P/N CP-16251; Varian, Inc.). The vendor supplies these tubes with approximately 100 mg of Tenax® TA sorbent material. We modified each of these tubes by replacing 15-mm of Tenax at the outlet end with an equal-length section of carbon molecular sieve (Carbosieve S-III, 60/80 mesh; P/N 10184; Supelco, Inc.). Sampling tubes were conditioned by He purge at 275 °C for 30-60 minutes before and between each use.

To ensure that samples contained quantifiable amounts of the target constituents, gas samples of varying volumes were withdrawn from a Tedlar bag and injected onto separate sampling tubes. Gas volumes used during the study generally ranged between 300 µL and 30 mL. The high concentrations of VOCs in two of the aerosol products (general purpose degreaser GPD-1 and spot remover SRM-1) necessitated further dilution of the products. This was accomplished by transferring aliquots of the first bags to secondary gas-filled bags. Specifically, 1 mL of gas was drawn from the initial bag by gas-tight syringe and injected into a second bag

with 1 L of nitrogen, yielding a 1:1000 dilution ratio. A gas sample of 1 to 20 mL then was drawn from the second bag and transferred to the sampling tube.

Product composition by solvent dilution

The composition of target VOCs in five products was determined by direct analysis of dilute methanol solutions of each of these products. A small aliquot of the liquid product (1.5-10 μL) was combined in a 5- or 10-mL conical volumetric vial with HPLC-grade MeOH. The vial was sealed and the solution was mixed by sonication or by gently shaking the vial by hand. An aliquot of the solution (2-35 μL) was withdrawn by syringe and injected onto a Tenax sampling tube. The tube was purged with He at 100 mL min^{-1} for 10-15 min to remove the MeOH. The sample was then quantitatively analyzed for individual VOCs by TD-GC/MS as described below. This facilitated the use of the same calibrations for both sample types.

Analysis of gas samples

Gas samples collected onto sorbent sampling tubes were qualitatively and quantitatively analyzed for VOCs of interest by thermal desorption-gas chromatography/mass spectrometry (TD-GC/MS). The samples were thermally desorbed and concentrated with an inletting system (Model CP-4020 TCT; Chrompack/Varian, Inc.). This system consists of a sample tube oven, a cryogenic concentrator with a Tenax-packed trap (P/N CP-16425; Varian, Inc.) to enhance recovery of very volatile compounds, and a control unit. The thermal desorption cycle included 5 min of He backflush with the tube heated to 50 $^{\circ}\text{C}$ (to remove water) and a 6.5 min period during which the sampling tube was heated to 235 $^{\circ}\text{C}$ over approximately the first 3.5 min and then held at this temperature. During backflush and tube desorption, the trap was cooled to -100 $^{\circ}\text{C}$. At the conclusion of tube desorption, the trap was rapidly heated to 225 $^{\circ}\text{C}$ and held at this temperature for 1 min to inject the sample onto the GC column.

The GC/MS analysis procedures generally followed EPA method TO-1 (USEPA, 1984). The GC (Series 6890A, Hewlett Packard Co./Agilent) was equipped with a 30-m long, 0.25-mm internal diameter, 1- μm film thickness DB-1701 chromatographic column (P/N 122-0733, Agilent). The GC oven was operated with the following temperature cycle: 1 $^{\circ}\text{C}$ held for 4.33 min, ramped at 5 $^{\circ}\text{C}/\text{min}$ to 225 $^{\circ}\text{C}$, and then held at 225 $^{\circ}\text{C}$ for 2 min. The MS (Series 5973 Mass Selective Detector, Hewlett Packard Co./Agilent) was operated in electron ionization mode. It was programmed to scan a mass range of 20 to 300 atomic mass units (amu) from 1.76 to 18 min and then a range of 35 to 350 amu for the remainder of the run. The GC/MS system was controlled and data analysis was performed with the manufacturer's software system (Model G1701BA, Version B.01.00; Hewlett Packard Co./Agilent).

Compounds present in air samples collected from the bags were identified using standard techniques. At the beginning of this task, we began to develop an electronic database of mass spectra and retention times for compounds known or expected to be major constituents of the cleaning products. These included compounds specifically listed on product MSDSs and labels and the major terpenoid constituents of pine oil. Pure compounds not already available in the laboratory were purchased from a commercial source (Aldrich, Sigma-Aldrich Corp.). Dilute solutions containing these compounds were prepared in methanol (MeOH). Small aliquots (1-10 μL) of the solution were injected onto sampling tubes containing Tenax only. The spiked compound masses generally were in the range of 25 to 100 ng. The tubes were purged with 100 mL min^{-1} of ultra-pure He for 5 min to remove the MeOH. The BFB internal standard then was added as described above. Compound mass spectra and chromatographic retention times were

entered into the database. Total-ion-current (TIC) chromatograms of samples of compounds volatilized from the cleaning products and the air fresheners were qualitatively analyzed by comparison of peaks in the samples with entries in this database using the GC/MS software system. Positive identifications were obtained when the mass spectra and retention times of the unknowns matched those of the pure compounds in the database. A National Institute of Standards and Technology (NIST) electronic database (Part No. 10236, WindowChem Software, Inc.) was used to tentatively identify additional compounds appearing in the chromatograms. If available, pure compounds consistent with these tentative identifications were purchased, analyzed, and their mass spectra and retention time data were added to our database. As described above, compound identifications were confirmed or rejected by comparison of the unknowns to the updated database. This process of confirming tentative compound identifications was conducted at the conclusion of the screening experiments (in late 2002 to early 2003), and again at the conclusion of the primary emission experiments (in late 2003 to early 2004) after reviewing samples from all products.

The predominant target compounds identified in the samples were quantified using multipoint calibrations created using the pure compounds. These calibrations were prepared by introducing varying concentrations and amounts of standard solutions in MeOH onto Tenax sampling tubes as described above. The calibrations for individual compounds spanned relevant ranges, from approximately 1 to several hundred nanograms. There were five or more individual masses or points in each calibration. Calibrations were constructed using extracted target ions with one or more qualifier ions to confirm compound identifications. The extracted target ion peak area and compound mass data were fit to a linear regression model with a zero intercept. All calibrations were referenced to the BFB internal standard (target ion $m/z = 174$), which was added to the standards and the air samples in equal amounts. Full calibrations were repeated throughout the study.

Compounds for which pure compounds were not available for use as standards were quantified using the TIC area responses of their peaks and the response relationship for a surrogate standard. d-Limonene (CAS 5989-27-5) was selected as an appropriate surrogate since most compounds in this category were terpenoids. First, a multipoint, linear regression calibration was prepared for d-limonene using the TIC area versus mass response of the peaks relative to the area versus mass response of the BFB internal standard (target ion $m/z = 174$). Then, the retention times of the compounds to be quantified were entered into the calibration and their masses were estimated using the same limonene area versus mass relationship. Thus, the reported masses of these compounds are limonene-equivalent masses. This procedure only could be applied to compounds that were chromatographically resolved from adjacent peaks.

Data quality and uncertainty

The study design incorporated a hierarchy of data quality checks. Several bags were prepared without products. Analysis of these blank bags using the same techniques as used for bags with products served as a check on the system blanks from bag preparation through analysis. For composition characterization, at least two replicate bags were prepared for each product using the same or similar dilution scheme. This procedure provided a measure of the reproducibility of the method from sample preparation through analysis. Approximately 25% of the prepared bags were sampled and analyzed in duplicate. This served as a measure of the reproducibility associated just with gas sampling and analysis. For two products, GPC-1 and GLC-1, three containers from different lots were purchased from different stores and analyzed.

These values represent the overall uncertainty of the bag method including potential variability among manufacturing lots. As noted, the bag method was intended to represent potential emissions of VOCs resulting from product use. Since the less volatile constituents of products may not completely volatilize or may sorb to bag surfaces or even gas-transfer syringes, the bag method values are expected to understate the actual fractional compositions for some compounds. To assess the magnitude of this bias, five products were analyzed by the solvent dilution technique.

For each product, the results for any duplicate analyses of a single bag were first averaged. Then, the values for the two sample bags (three bags for product GPC-4) prepared from a single product container were averaged. Relative deviations between duplicate bags were calculated as the absolute difference divided by the average value expressed in percent. For products GPC-1 and GLC-2, the results for each set of duplicate bags were averaged and then the average and standard deviation was calculated for the three containers. A relative standard deviation was calculated as the quotient of the standard deviation and the average expressed in percent.

Calculation of product composition

Concentrations of the target VOCs in the products, determined as mass fractions, were calculated using equation 3-1.

$$C_i = \frac{M_{i,GC}}{V_S} \times \frac{V_{bag}}{M_{CP}} \quad (3-1)$$

In this equation, C_i is the mass fraction of compound i in the product, $M_{i,GC}$ is the mass of compound i determined from TD-GC/MS analysis of the gas sample withdrawn from the Tedlar bag containing the vaporized product, V_s is the gas sample volume, V_{bag} is the total gas volume in the bag, and M_{CP} is the mass of the cleaning product introduced into the bag. The mass of a liquid cleaning product was estimated from the introduced volume assuming a product density of 1 g cm^{-3} . Complete volatilization of the product in the bag was assumed. Mass fraction values reported in data tables are expressed as percentages.

3.3.3. Screening results

Target compounds

Quantitative product composition data were generated for ethylene-based glycol ethers, unsaturated terpenoid compounds, other unsaturated compounds that are potentially reactive with ozone, and combined xylene isomers. The compounds in these chemical classes with mass fraction compositions determined by the bag method of $\geq 0.01\%$ in one or more of the 21 products are listed in Table 3.8. The chemical structures of the compounds in the first three categories are shown in Figures 3.1-3.3. These consisted of 10 unsaturated terpene hydrocarbons (Figure 3.1), 12 oxygenated compounds including terpenoids with unsaturated C-C bonds (Figure 3.2), and two glycol ethers (Figure 3.3). The compounds are listed in order of increasing chromatographic retention time within each of these classes. Some of the compounds (α -phellandrene and four terpineol isomers) were tentatively identified based on high quality matches (typically $>85\%$) of their mass spectra with mass spectra in the NIST electronic library. The identifications of the other compounds were confirmed. Reported second-order rate constants for the reactions of the terpene hydrocarbons and linalool with ozone as discussed in §2.5 also are shown in the table. Rate constants for the other unsaturated compounds are not

readily available from the published literature. Ten of the target VOCs were quantified using their TIC areas with d-limonene as the surrogate standard. The other VOCs were quantified using calibrations prepared from pure compounds.

Several additional compounds were detected as discussed below. Isopropyl alcohol (2-propanol), a chemical of potential concern, was found in three general-purpose cleaners. It is listed as a Category IIb chemical in the TAC list. This designation indicates that it is a substance not identified as a TAC, but rather is known to be emitted in California and has one or more health values under development by the California Office of Environmental Health Hazard Assessment (OEHHA). In fact, there is both an acute and a chronic reference exposure level (REL) for isopropyl alcohol (OEHHA, 1999 and 2000). Isopropyl alcohol was not included among the target compounds quantified in this study, as it is a very volatile compound that is difficult to reproducibly measure by the selected method.

Reproducibility of bag method

The overall reproducibility of the measurements of VOC mass fractions across the three different containers and lots for general purpose cleaner GPC-1 and glass cleaner GLC-1 are shown in Tables 3.9 and 3.10, respectively. The results for the VOCs volatilized from GPC-1 indicate a reproducibility of about 15% or better for all target analytes except α -pinene and β -pinene (Table 3.9). For GLC-1, the reproducibility for the measurement of the two glycol ethers was better than 5% for 2-butoxyethanol (2-BE) and better than 10% for 2-hexyloxyethanol (2-HE) (Table 3.10).

The uncertainty associated with gas sampling and analysis was estimated by examining the results for replicate samples collected from bags. Ten bags containing a cleaning product and two bags containing an air freshener were sampled and analyzed in duplicate or (for one cleaning product) in triplicate. (See Appendix B, Tables B.1-B.7.) For d-limonene and 2-BE, the two major cleaning product constituents, there were four and seven sets of replicate samples, respectively. The mean relative deviation for d-limonene was 6% (range: 1%-16%); and the mean relative deviation for 2-BE was 10% (range: 1%-44%). For α -terpineol, a major constituent in pine-oil based cleaners, the relative deviation was 9% ($n = 1$ pair). For air freshener AFR-3, the average relative deviations ($n = 2$ pairs) for the three constituents, d-limonene, dihydromyrcenol and linalool, were 51%, 7% and 4%, respectively.

The reproducibility of the method from sample preparation through analysis was estimated by examining the results for the replicate bags. Again considering the same major constituents of cleaning products, there were eight sets of replicate bags for d-limonene, eight replicated bags for 2-BE and two replicated bags for α -terpineol. For these three chemicals, the respective average deviations were 8% (range: 0-19%), 20% (range: 0-75%), and 17%. The four major constituents of air fresheners were d-limonene, dihydromyrcenol, linalool, and linalyl acetate with two or four sets of replicate bags each. The average relative deviations were limonene 24% (range: 0-69%), dihydromyrcenol 46% (21 and 72%), linalool 24% (range: 0-72%), and linalyl acetate 14% (3 and 24%). The high variability in the analyses of d-limonene, dihydromyrcenol, and linalool in air fresheners was attributed to difficulties encountered in the analysis of the two bags of AFR-3 (Table B.7). This may have been due to the gel product form and the difficulty of accurately weighing and transferring the product to the bags.

Mass fractions of target VOCs in products

The mass fractions of VOCs for the 21 products are presented in Tables 3.11-3.15. The products first were segregated into groups based on product type (i.e., cleaning products and air fresheners) and then the cleaning products were further segregated by their dominant chemical composition characteristics. The results for four cleaning products with mass fractions of d-limonene exceeding 3% are shown in Table 3.11. The results for three pine oil based cleaning products are shown in Table 3.12. The results for cleaning products containing greater than 0.5% 2-butoxyethanol are shown in Table 3.13. The compositions of cleaning products containing less than 0.2% of the target compounds are presented in Table 3.14. The results for the four air freshener products are presented in Table 3.15. The mass fraction results for each sample collected from each individual bag that was prepared from one or more product containers are shown in Appendix B, Tables B.1-B.7, along with the preparation information for these samples. The products are listed in Tables B.1 through B.7 in approximately the same order they are presented in Tables 3.11 through 3.15.

Blank bags did not contain detectable amounts of the compounds of interest; thus, no background corrections were required. In the data tables, values for which the relative deviation was greater than 50% are identified. The relative deviation for all other values was less than 50%. The lower reporting limit for individual VOCs was established at a mass fraction in the product of 0.01%.

Four cleaning products used d-limonene as a solvent: a general-purpose degreaser (GPD-1), a general purpose cleaner (GPC-4), a multi-purpose solvent (MPS-1), and a furniture maintenance product (FMP-1) (Table 3.11). GPC-4 also contained 2-butoxyethanol as a solvent at greater than 1% mass fraction (Table 3.13). The highest d-limonene mass fraction of 25% occurred in GPD-1, an aerosol spray product. The MSDS for this product lists cold pressed orange oil (CAS No. 8028-48-6) as the main ingredient. Orange oil is approximately 90% d-limonene. The only other terpene hydrocarbons detected in the four products by the bag method were α -pinene, β -pinene, and β -myrcene.

Three general-purpose cleaners (GPC-1, GPC-6 and GPC-7) contained the constituents of pine oil (Table 3.12). Most pine oil in use today is synthetically produced by the acid-catalyzed hydration of pinene (FFHPVC, 2001). Tertiary terpenoid alcohols dominate the composition of synthetic pine oil. The major constituent is α -terpineol (approximately 50-60% by weight). Other reported constituents are additional tertiary alcohols including γ -terpineol, β -terpineol, and 4-terpineol; secondary terpenoid alcohols; terpene hydrocarbons including d-limonene; and aromatic and alicyclic terpene hydrocarbons and ethers.

Fourteen unsaturated pine oil constituents were detected with mass fractions $\geq 0.01\%$ in the three products. For product GPC-1, the average results for each of the three containers are shown. Product GPC-7 contained the same constituents in about the same ratios but with approximately four-fold lower mass fractions. The composition of pine oil constituents in GPC-6 was distinctly different, with α -terpineol having a much lower mass fraction relative to d-limonene and terpinolene than in the other two products.

Six cleaning products utilized 2-butoxyethanol as a solvent (Table 3.13). The mass fractions of 2-butoxyethanol ranged from about 0.6 to almost 10%. As noted, product GPC-4 also contained d-limonene. Glass cleaner GLC-1 also contained 2-hexyloxyethanol as a solvent. The mass fraction of 2-hexyloxyethanol was approximately 40% of the value for 2-butoxyethanol.

Five cleaning products exhibited only relatively low amounts of the target VOCs by the bag method (Table 3.14). General cleaning product GPC-5 and wood cleaner WDC-1 exhibited small amounts of a single target compound, either d-limonene or dihydromyrecenol. The composition of the target VOCs in furniture maintenance products FMP-3 and FMP-4 was nearly identical. The primary compound quantified in the bag samples was d-limonene, possibly used to impart a fragrance to the products. Citral, which was found in both of these products, is a fragrance chemical often used to impart a citrus or “lemony” odor. Furniture maintenance product FMP-2 contained xylenes with a mass fraction of 0.07% for combined ortho-, meta-, and para- isomers.

The compositions of the target VOCs in the four air freshener products as determined by the bag method are listed together in Table 3.15. Products AFR-1, AFR-2, and AFR-3 are either oily or gel-like mixtures of fragrance chemicals that are dispensed to room air by a plug-in electrical vaporizer. Product AFR-4 is an aerosol spray product. Linalool was the predominant compound in the vapor phase of the three plug-in air fresheners with mass fractions ranging from 4% to almost 9%. d-Limonene also was present in these products with a mass fraction near 1%. Dihydromyrecenol and linalyl acetate each were among the predominant ingredients in two of the three plug-in products. The mass fractions of the target VOCs in the aerosol product were low by comparison to the other products.

The results for the mass fractions of d-limonene and the summed mass fractions of compounds with unsaturated C=C bonds potentially reactive with ozone are summarized for nine cleaning products and three air fresheners in Table 3.16. The other products either lacked these compounds or contained them at relatively low abundance with the total fractional sum being less than 0.1%. For five of the cleaning products listed in the table (GPD-1, GPC-4, FMP-1, FMP-3 and MPS-1), d-limonene comprised all or more than two-thirds of the ozone-reactive compounds in the products. For the air fresheners, d-limonene comprised about 10% of the total ozone reactive compounds.

Additional abundant compounds in products

The bag samples for all 21 products were qualitatively assessed for relatively abundant compounds not within the classes of VOCs of primary interest to this study. Table 3.17 lists the additional abundant compounds detected in the bag samples of the four air fresheners and ten of the 17 cleaning products. The remaining seven cleaning products either did not contain significant amounts of VOCs or their compositions were clearly dominated by compounds of interest to the study as described. None of these additional compounds were quantified. Isopropyl alcohol (2-propanol) is a compound of potential interest, but could not be reproducibly quantified by the method. In addition, a single approximate peak height cutoff point was applied across all bag samples to determine the inclusion of a compound in the list without adjustment for product dilution. Thus, the reader is cautioned that the cutoff point as it would relate to mass fraction in the product is not uniform across the products.

Two general purpose cleaners utilizing pine oil as an ingredient (GPC-1 and GPC-7) also contained 2-propanol (isopropyl alcohol, CAS No. 67-63-0) as did glass cleaner GLC-1. Both general purpose cleaners GPC-4 and GPC-5 contained a mixture of di(propylene glycol) butyl ethers (CAS No. 35884-42-5).

All four furniture maintenance products and the multi-purpose solvent MPS-1 contained hydrocarbon mixtures as principal ingredients; the boiling point ranges of these solvents varied among the products. Products FMP2, FMP-3 and FMP-4 contained hydrocarbons (alkane,

alkene and cyclic hydrocarbons) in the carbon range of C₇ to C₉. Product MPS-1 contained hydrocarbons in the range of C₁₀ to C₁₃. Product FMP-1 principally contained C₁₃ to C₁₅ branched alkane hydrocarbons. The two aerosol furniture maintenance products (FMP-3 and FMP-4) were similar in composition for their content of target VOCs (as noted above) and hydrocarbons solvents; they also contained octamethylcyclotetrasiloxane (CAS No. 556-67-2) and other siloxane compounds.

The compositions of the plug-in air freshener products (AFR-1, AFR-2, and AFR-3), as determined by analysis of the bag samples, were relatively complex. Many of the detected compounds likely are present to impart fragrance to the products. The additional abundant VOCs listed in Table 3.16 for these products primarily are oxygenated compounds consisting of alcohols and esters. Product AFR-2 contained di(propylene glycol) butyl ethers. Aerosol spray air freshener AFR-4 contained butylated hydroxytoluene (BHT, CAS No. 128-37-0).

Comparative evaluation of measured VOC mass fractions

Manufacturer Material Safety Data Sheets (MSDSs) listing target VOCs as principal ingredients were obtained for six of the 21 cleaning products and air fresheners. The two compounds disclosed in these MSDSs were 2-butoxyethanol and d-limonene typically listed as orange oil or concentrated orange oil. In Table 3.18 the product mass fractions of d-limonene and 2-butoxyethanol determined by the bag method are compared to the values in their corresponding MSDSs. With one exception, the measured values were within the manufacturers' specified limits. For general purpose degreaser GPD-1, the d-limonene measured value exceeded the specified 20% value for orange oil by 5%. The difference is actually larger considering that d-limonene comprises approximately 90% of orange oil.

The compositions of products GPC-1, GPC-3, GPC-4, DIS-1 and GLC-1 were characterized by direct analysis of these products diluted in methanol. Note that additional solvent dilution results including values obtained for multiple containers collected over time are reported for four of these products in §3.4. The solvent dilution and bag method results are compared for general-purpose cleaners GPC-1 and GPC-4 in Table 3.19. The results obtained by the two methods are in good qualitative and semi-quantitative agreement. The principal difference observed primarily for GPC-1 is that the solvent dilution method yielded up to five-fold higher values for the unsaturated oxygenated compounds. Generally, these are the less volatile, more polar, and more sorptive of the quantified VOCs. The lower values by the bag method may reflect incomplete volatilization or losses of less volatile compounds to the surfaces of the bags or during the gas-sample transfer process.

The fractional compositions of 2-butoxyethanol and 2-hexyloxyethanol in products DIS-1, GPC-3 and GLC-1 as determined by solvent dilution and the bag method are compared in Table 3.20. Overall, the results for the glycol ethers in these three products were similar by the two methods.

3.3.4. Estimates of potential residential emissions of target VOCs

The results of the product screening experiment were applied in a modeling exercise as a partial basis for selecting products for the primary emissions experiments conducted under simulated-use conditions as described in §3.4. Products were selected that are widely available in California and whose regular use might lead to substantial indoor air concentrations of 2-

butoxyethanol and other ethylene-based glycol ethers or unsaturated terpenoid compounds that can react readily with ozone.

We used VOC mass fraction data in combination with the manufacturers' product label information describing product use and application procedures, assumptions regarding consumer use patterns, and estimates of product use rates to predict the possible total emission rate of the VOCs of interest for routine product use in households. This exercise was designed to provide comparative information on the potential of the products to affect residential indoor air quality. The intent was to provide indications of scale, rather than precise results.

Labels on cleaning products typically describe the manufacturers' intended uses and provide directions for their application. Using the labels as a guide, we summarize the possible consumer uses of the 17 cleaning products during house cleaning in Table 3.21. Although disinfectant DIS-1 and general purpose cleaner GPC-4 are commercial products, they were sold in retail stores and residential consumers might purchase and use them in kitchens and bathrooms on a routine basis. The spot remover (SRM-1) and the multi-purpose solvent (MPS-1) likely are used only occasionally or infrequently. It is reasonable to assume that the remaining cleaning products are used routinely, either weekly or daily for some products.

Three of the cleaning products (DIS-1, GPC-3, and GPC-4) are sold in trigger spray bottles, but their labels recommend dilution for at least some applications. Using the labels as a guide, we list in Table 3.22 the likely dilutions by cleaning task for these three products and for the other three liquid products that have recommended dilutions. For DIS-1, the manufacturer recommends 1/16 dilution for cleaning floors. For GPC-3, the manufacturer recommends 1:10 dilution for most cleaning applications, 1/30 dilution for cabinets, paneling, and non-wood floors, and full strength use for ovens and range hoods. For GPC-4, the manufacturer recommends the product be used at half strength for most applications and at 1/20 dilution for cabinets, paneling and non-wood floors. However, because the products are packaged in trigger spray bottles, it is reasonable to assume that some consumers use the products at full strength for many applications. The other three cleaning products listed in Table 3.22 (GPC-1, GPC-6 and GPC-7) are liquids intended for use at substantial dilution (1/32 or 1/64) for most applications.

Clearly there are large variations in the sizes and layouts of residences in California and elsewhere. For the purposes of this exercise, we selected a relatively small, detached single-family residence as the prototype. A scaled floor plan was obtained for a single-story manufactured house with a total floor area of 140 m² (1,500 ft²) consisting of three bedrooms and two bathrooms. This size and layout is typical of many older single-family houses in California and also may be representative of units in multi-family dwellings. Using the floor plan drawing, we calculated the areas of the house features that would be cleaned routinely. Wood furniture surface area was estimated based on measurements made in the home of one member of the research team. These areas are listed in Table 3.23.

Cleaning product use rates for undiluted or diluted products were estimated per area of surface cleaned. Initial use-rate estimates of use rate were based on the measured amounts of products used by a single technician to simulate cleaning of a measured area of countertop in the laboratory. These use rates were 8.6 g m⁻² for a trigger spray product and 6.1 g m⁻² for an aerosol spray. A subsequent survey of multiple subjects (described in §3.4) determined a trigger spray use rate of 10.8 g m⁻². For this exercise, we selected a use rate of 10 g m⁻² for both routine house cleaning and specialized cleaning activities with liquid products and 6 g m⁻² for aerosol products. We assumed diluted liquid floor cleaning solutions (Table 3.22) were applied at 10 g m⁻².

We estimated the use rate (grams per use) for each cleaning product for a complete house-cleaning event (e.g., kitchen, bathrooms, and cabinets) assuming the product was used for all of the purposes indicated in Table 3.21. These rates rounded to the nearest 5 g are shown in Table 3.24 for 14 cleaning products. General purpose cleaner GPC-5, wood cleaner WDC-1, and furniture maintenance product FMP-2, were omitted from the analysis because they did not contain significant amounts of the target compounds. For screening purposes, the potential emission of total unsaturated VOCs and ethylene-based glycol ethers during a house-cleaning event was estimated as the product of the use rate and the mass fractions of the compounds of interest determined by the bag method. Alternate potential emissions of VOCs assuming full strength application for all tasks are shown in parentheses for products GPC-3 and GPC-4.

The estimated VOC emission rates (grams per use) represent a high-end situation in which a single cleaning product is used for all possible applications and all VOCs of interest in the product are completely volatilized during use. Also, it is noted that the estimated total amount of product used in this exercise represents a substantial fraction of the amount included in a standard consumer container (typically 650 to 1000 mL). Nevertheless, the exercise serves as a useful basis for a relative comparison of the potential impacts of the products.

Ten of the cleaning products were estimated to have potential emissions of VOCs of interest greater than or equal to one gram per use. (Compare with the 0.5 g emission assumed for Figures 2.1 and 2.2.) The products with the highest estimated emissions (> 5 g/use) of ozone-reactive VOCs are a general-purpose degreaser (GPD-1), two general-purpose cleaners (GPC-2 and GPC-4), a furniture maintenance product (FMP-1), and a multi-purpose solvent (MPS-1). The products with the highest estimated emissions (> 5 g/use) of ethylene-based glycol ethers are a disinfectant (DIS-1), a general-purpose cleaner (GPC-2), and a spot remover (SRM-1).

For the three plug-in air fresheners, product emissions were assumed to be constant. Product use rates were estimated to be 5 grams per week for the oily liquids (AFR-1 and AFR-2) and 1.2 grams per week for the gel (AFR-3). From these assumptions, AFR-1 and AFR-2 are predicted to have the highest potential emissions per week of ozone reactive VOCs. However, these rates are less than one gram per week.

3.4. Emissions and Concentrations from Simulated-Use Experiments

3.4.1. Introduction

The indoor use of cleaning products and air fresheners leads to inhalation exposures to primary emissions of volatile product constituents and to secondary pollutants formed as these constituents react (e.g. with ozone) in the indoor environment. Certain of these inhalation exposures raise potential health concerns, as reviewed by Wolkoff et al. (1998) and in §2.

One class of compounds for which exposure concerns arise is ethylene-based glycol ethers, which are widely used as solvents in cleaning products. The US Environmental Protection Agency classified ethylene-based glycol ethers as hazardous air pollutants (HAP) under the 1990 Clean Air Act Amendments. The agency recently delisted 2-butoxyethanol (2-BE, CAS No. 111-76-2, also known as ethylene glycol monobutyl ether) from the HAP group of glycol ethers. The action was substantiated by the agency's determination that "emissions, ambient concentrations, bioaccumulation, or deposition of [2-BE] may not reasonably be anticipated to cause adverse human health or environmental effects" (USEPA, 2003 and 2004a). The exposure assessment used to support the decision considered only inhalation exposure owing to emissions to *ambient* air. The potentially higher concentrations and exposures associated with 2-BE emissions from products used *indoors* were not addressed.

The California Air Resources Board lists ethylene-based glycol ethers as toxic air contaminants (TACs). Within its TAC identification program, California has established reference exposure levels (REL) for several specific glycol ethers, including 2-BE with a value for acute (1-h) exposures of 14 mg m^{-3} to protect against eye and respiratory irritation (OEHHA, 1999). The federal reference concentration for chronic inhalation exposure (RfC) is 13 mg m^{-3} , with changes in red blood cell count as the critical effect (<http://www.epa.gov/iris/subst/0500.htm>).

Also of potential concern in cleaning products and air fresheners are terpene hydrocarbons, terpene alcohols, and other related unsaturated compounds. These chemicals, frequently derived from plant oils, are used as scenting agents in many consumer products and as active solvents in certain cleaning products. Many of these compounds react rapidly with ozone, producing formaldehyde (Fan et al., 2003), hydrogen peroxide (Li et al., 2002), hydroxyl radical (Weschler and Shields, 1997a), and secondary organic aerosol (Weschler and Shields, 1999; Wainman et al., 2000; Liu et al., 2004; Sarwar et al., 2004). Recent studies suggest that reactive chemistry between terpenes and ozone produces upper airway and eye irritants (Wolkoff et al., 2000; Klenø and Wolkoff, 2004).

Relatively little is known about the chemical emissions and constituent gas-phase concentrations that result from the use of cleaning products and air fresheners. Gibson et al. (1991) conducted simulated-use experiments to characterize emissions and concentrations of diethylene glycol monobutyl ether from hard-surface cleaning products. Zhu et al. (2001) used small-chamber experiments to characterize emissions of 2-BE from selected consumer products, including some cleaning products. Wainman et al. (2000) reported concentrations of d-limonene from simulated use of a lemon-scented furniture polish. Several groups have investigated the secondary particle production associated with terpene-ozone interactions in which the terpenes were emitted from use of air fresheners or cleaning products (Wainman et al., 2000; Sarwar et al., 2004; Liu et al., 2004).

In this section of the report, we document original experiments investigating the indoor air emissions and concentrations of ethylene-based glycol ethers, terpenes, and related compounds associated with cleaning product and air freshener use. For six commercial products, the chemical composition was measured directly and a series of simulated use experiments was conducted. In these experiments, time-dependent concentrations of target constituents were measured, and associated time-integrated emissions were calculated.

3.4.2. Methods

Product selection

The six products studied were selected using a multistage screening process, considering the following key criteria. (1) Products are readily available to consumers through retail outlets. (2) Products are either known or expected to contain substantial levels of reactive terpenes, terpene alcohols, other unsaturated compounds, or ethylene-based glycol ethers. (3) The set of products includes at least one each of glass cleaner, general-purpose cleaner, and air freshener.

As described in §3.2, in the first stage, a shelf survey of cleaning products and air fresheners was conducted in five chain retail outlets in the San Francisco Bay Area. From the resulting list, we selected fifty candidate products and reviewed product labels and available material safety data sheets to determine or infer the presence of target constituents. As detailed in §3.3, twenty-one of the products subsequently were experimentally screened to identify and semi-quantitatively determine their chemical compositions. These measurements were made by

means of volatilizing small aliquots of the products into Tedlar bags and sampling the air in the bags. Six products were selected from this group for further study. Summary information for the selected products is presented in Table 3.25. These products include one glass cleaner (GLC-1), four general-purpose cleaners (GPC-1 through GPC-4), and one scented-oil air freshener (AFR-1). In Appendix C are tables documenting the place and date of purchase for the products (Table C.1) and indicating the relationship between the specific purchased products and the resulting experimental measurements (Table C.2).

Composition determination by solvent dilution

To complement the bag method analyses described in §3.3, product composition was determined by analysis of a dilute solution of each product in methanol. A small aliquot of the liquid product (1.5-10 μL) was combined in a volumetric, conical vial with 5-10 mL HPLC-grade methanol. The vial was sealed then sonicated or shaken gently by hand. An aliquot of solution (2-35 μL) was withdrawn by syringe and injected into a Tenax tube under a 100 mL min^{-1} He purge maintained for 10-15 min to volatilize the methanol. The sample was then analyzed as described in §3.3.2.

Experimental chamber and materials

Simulated-use experiments were conducted in a 50- m^3 chamber designed to represent a room in a typical residential environment. Construction materials include wood framing with plywood underlying the floor, two walls and the ceiling. The chamber walls and ceiling are finished with 64 m^2 of gypsum wallboard coated with low-VOC paint. The plywood subfloor is covered with aluminum sheeting. For this study, a portion of the floor (3.9 m^2) was covered with vinyl composition tiles to provide a surface for mopping. Molding was attached at the tile perimeter to contain cleaning solution. A laminate table with top surface area of 1.16 m^2 was placed in the middle of the room.

Chamber air was mixed with four small axial fans mounted at 1/3 and 2/3 of ceiling height on poles 1 to 1.5 m from room corners. Ventilation was mechanically provided, with outdoor air passed through a bed of activated carbon to remove organic gases and ozone. The air-exchange rate was fixed and checked during each experiment by measuring the concentration decay of injected sulfur hexafluoride (SF_6) tracer gas. Temperature in the chamber was controlled by thermostatic regulation of the air temperature of the building in which the chamber is contained. Relative humidity (RH) was not controlled, but experiments were limited to days in which RH was in the range of 40-70% at the start. Temperature and RH were measured continuously using Vaisala sensors; output was recorded as 1-h averages.

Application protocols

Table 3.26 summarizes the 18 simulated-use experiments conducted in the 50- m^3 chamber. The protocols outlined in Table 3.26 were developed to simulate two general methods of product use: (1) full-strength application, and (2) dilute solution use. Three of the general-purpose cleaners (GPC-1, GPC-3 and GPC-4) instruct use at varied levels of dilution depending on application, including full-strength use for tough jobs or as needed. Two of these (GPC-3 and GPC-4) implicitly encourage full-strength use as they are packaged in trigger-spray bottles. These three products were evaluated in both full-strength and dilute form. GLC-1 and GPC-2 are packaged in trigger spray bottles that recommend full-strength use on a variety of surfaces; these

products were evaluated exclusively in a full-strength application. The scented-oil air freshener was used as directed.

The full-strength surface cleaning protocol was designed to simulate varied applications including cleaning, degreasing and/or disinfecting of hard surface counters, tabletops, stovetops, or glass. Products were applied full-strength to a 0.56-m² section of the laminate tabletop, providing a cleaning surface to room volume ratio of ~0.01 m² m⁻³. Four products (GLC-1, GPC-2, GPC-3, and GPC-4) were dispensed by spraying ~6 mL (~11 g m⁻²) from the product container. For GPC-1, ~10 mL (~18 g m⁻²) was dispensed by pipette. These amounts are intended to represent high but realistic use rates, based on the results of product-use surveys (see following subsection: “product application rates”). After application, the product was left undisturbed for ~1 min. In two experiments (1L and 1M; see Table 3.26), the wetted surface was wiped clean with paper towels. In other experiments, the surface was scrubbed using a wetted and loosely wrung 114 × 68 × 15-mm cellulose sponge backed with abrasive material (3M Scotch-Brite® heavy-duty scrub sponge). After scrubbing, the tabletop was dried with paper towels and the sponge was rinsed in a bucket of clean, warm water (T = 45-55 °C). Next, water was applied to the tabletop with the sponge to simulate rinsing. Finally, the tabletop was dried with a second set of paper towels. In experiments 1A-1D, the paper towels were removed from the chamber upon completion of the cleaning activity. In experiments 1E-1M, paper towels were deposited in a wastebasket with plastic liner and remained in the chamber for 24 h. The full application procedure, including scrub, wipe, rinse, and wipe steps was completed in approximately 2.5 min during experiments 1A-1D and 3.5 min in experiments 1E-1K. The spray and wipe procedure (experiments 1L-1M) was completed in 2 min.

Materials were weighed before and after each use starting with experiment 1E. The wetted sponge was wrung to a mass of 56±2 g (μ±σ) before scrubbing and weighed 50±2 g after use; a net 6±3 g of water thus was transferred from the sponge to the cleaning surface during this step. The paper towels used after scrubbing absorbed 9±2 g of solution. The rinse sponge weighed 61±6 and 52±3 g before and after use, delivering 9±3 g of solution. The paper towels used after rinsing absorbed 7±2 g of solution. By the end of experiments in which paper towels remained in the chamber, those used after scrubbing and rinsing retained 1.9±1.4 and 0.5±0.3 g, respectively.

The second protocol was intended to represent general use of dilute cleaning solutions. The protocol included solution preparation, wet mopping, and dry mopping of floor tiles. The 3.9 m² area of tiles provided a cleaned surface to room volume ratio of ~0.08 m² m⁻³. The solution was prepared inside the chamber by measuring and dispensing the designated amount of full-strength cleaner (experiments 1N-1Q) into ~4 L of warm water (T = 45-55°C) in a 10 L plastic bucket. A 2-layer sponge mop (Quickie Home Pro) measuring 223 × 87 × 25 mm was used to spread the solution while applying pressure to simulate cleaning. Six mop strokes (back and forth) were used to apply the solution to each quadrant of the floor. The mop was submerged then removed and tilted to drain excess solution before mopping each quadrant. The wrung mop was used to soak up solution in 24 half-strokes; additional wringing occurred after each 4-6 strokes. Finally the mop was wrung and guided over the entire tiled area to complete the dry-mopping phase. The remaining solution was poured into a second bucket within the chamber to simulate disposal. The procedure lasted ~7-7.5 min and ended with the removal of all cleaning materials from the chamber. The net amount of solution used during cleaning was ~90-120 g, corresponding to ~2-3% of the prepared mopping solution.

In experiment 1R, the scented oil air freshener was plugged into an extension cord mounted to one of the table legs. The product container was weighed at elapsed times of 2, 8, 21, 29, 51, and 73 h after use began.

Product application rates

Two surveys were conducted to determine appropriate product application rates. Subjects were recruited from LBNL staff via e-mail, telephone and personal invitation. In the first survey, each of 25 subjects was instructed to use a trigger-spray product (GPC-3) to clean a 0.93 m² (10 ft²) section of laminate tabletop. Although the tabletop was clean, subjects were asked to imagine it to be “moderately dirty,” e.g. after preparing dinner, but having no “caked-on food or stains that would result from weeks or months without cleaning.” The tabletop was wiped completely dry between subjects. A single observer provided instruction, recorded the mass of the bottle before and after use and the number and approximate extent of trigger pulls for each subject. The second survey measured the application rate of two disinfection products, including GPC-1. Each of 11 subjects was instructed to use the products to disinfect two identical, clean, laminated tabletops, each having top dimensions of 61 × 191 cm for a surface area of 1.16 m² (12.5 ft²). Subjects were provided with an almost full bottle of each product and encouraged to review the directions. Also provided was a bucket of clean water, a sponge, and paper towels. An observer weighed the product bottle before and after each use and recorded subject comments. The table and sponge were rinsed and dried between subjects.

VOC sampling and chemical analysis

Air samples for analysis of volatile organic compounds (VOCs) were collected onto sorbent tubes (P/N CP-16251, Varian Inc.) packed with Tenax TA and Carbosieve SIII or with Tenax TA only. Air was drawn directly onto the sorbent tubes, which were fixed horizontally at least 30 cm from the chamber wall. Background samples were collected before each experiment at ~100 cm³ min⁻¹ over 20-40 min. Experimental samples were collected at 1.8-5.5 cm³ min⁻¹ using peristaltic pumps (Cole-Parmer); flow rates varied by <1% based on measurements throughout the study. For cleaning product experiments, integrated samples were resolved at least to the following schedule: 0-10, 10-30, and 30-60 min; and 1-2, 2-4, and 4-24 h from the start of the experiment. Sampling periods were further subdivided as needed to achieve sample masses within quantitation ranges. Samples were collected in duplicate, and pairs were analyzed for at least 1-2 periods of each experiment. For the air-freshener experiment, samples of 2-5 min duration were collected periodically over three days beginning with the start of use.

Samples were analyzed by thermal desorption gas chromatography with mass selective detection and quantitation (TD-GC/MS) as described in §3.3.2 and as previously reported (Singer et al., 2004). Samples were analyzed on the day of collection or stored in a freezer for up to a few days before analysis. Most analytes were quantified using multipoint calibration curves developed from pure compounds (Aldrich). Quantitation was referenced to an internal standard of 1-bromo-4-fluorobenzene. Analytes for which standards could not be obtained were identified using spectral libraries and quantified by total ion current, based on the instrument response to d-limonene.

Emission factors

Effective emission factors (i.e., mg of constituent emitted per g of total product used) were determined for major analytes by material-balance analysis. The key concept is that the

effective net mass emitted into air is ultimately balanced by the mass removed from the chamber by means of ventilation. Since the chamber was continuously well mixed, the removal rate is determined as the time-integral of the product of the background-corrected chamber air concentration ($\mu\text{g m}^{-3}$) times the ventilation rate ($\text{m}^3 \text{min}^{-1}$). For the cleaning-product experiments (1A-1Q), mass emissions were determined using time-averaged concentration data for a 24-h period beginning with product use. Mass emissions so determined were normalized to the quantity of product dispensed. Fractional emissions of analytes (i.e., g emitted per g dispensed) also were computed, utilizing the composition data. For the air freshener experiment (1R), time-average analyte concentrations were estimated for the three days of product deployment using linear interpolation between points; these results were used to determine effective emission rates in units of mg d^{-1} .

Emission factors are termed “effective” as they reflect the net result of emissions and material interactions including emissions from paper towels, desorption from cleaned surfaces, and net sorptive uptake to other chamber surfaces such as wallboard.

Data quality and uncertainty

Data quality checks for the primary emissions experiments followed a similar hierarchy as described for the screening experiments. VOC samples were collected prior to the start of each experiment to quantify chamber air concentrations of product constituents resulting from residual desorption of mass that had sorbed during previous experiments. These concentrations were subtracted from those measured during all periods following introduction of cleaning products. This assumes that desorption of previously sorbed mass continued at the same level throughout each experiment. The potential effect of this assumption on the calculated emission factors was estimated. Samples were collected in duplicate for all sampling periods; both samples were analyzed from at least one pair, and usually two pairs in each experiment. Duplicates selected for analysis were drawn from various sampling periods across experiments to evaluate precision across a range of mass collected and gas-phase concentrations. Two cleaning scenarios were studied in replication – surface cleaning with GPC-3 (experiments 1F-1H) and surface cleaning with GPC-4 (experiments 1I-1K) – to investigate repeatability associated with experimental protocols.

3.4.3 Results and discussion

Product composition

Product composition results are summarized in Tables 3.27-3.29. More detailed composition data are presented in Appendix C, Tables C.3-C.9. (We refer the reader to Table 3.7 for a mapping of the product codes to a complete list of tables in which composition data are presented.)

Among the six products, four contained 2-BE at mass concentrations of 6-62 mg mL^{-1} . The highest concentration of 2-BE was in GPC-3, which is a “concentrated” product sold in both trigger spray and screw-top bottles. Anecdotal reports of survey subjects suggest that the product often is used at full-strength to clean hard surfaces. The glass/surface cleaner contained both 2-BE and 2-hexyloxyethanol (2-HE, CAS No. 112-25-4, also known as ethylene glycol monohexyl ether) at concentrations of 6 and 4 mg mL^{-1} , respectively. GPC-4, marketed as a degreaser and cleaner and sold in a trigger spray bottle, contained both 2-BE and d-limonene at levels of 31 and 44 mg mL^{-1} , respectively.

GPC-1 is a pine-oil based cleaner that contains 11 terpenoids including both terpene hydrocarbons and alcohols (plus at least two additional VOCs) at mass concentrations exceeding 1 mg mL^{-1} (Table 3.28). Several of these identified constituents are known to react rapidly with ozone. The reaction between d-limonene and ozone to form secondary pollutants has been well documented (see §2.5 and Table 2.8). Terpinolene has an ozone reaction rate that is roughly an order of magnitude higher than that of d-limonene and is present in GPC-1 at a higher mass fraction. α -Terpinene is present at a much lower mass fraction but reacts with ozone about two orders of magnitude faster than does d-limonene. α -Terpineol, which comprises almost 7% of GPC-1, reacts with ozone at a rate comparable to that of d-limonene.

The air freshener contained six unsaturated and several saturated VOCs at levels above 6 mg mL^{-1} (Table 3.29). Linalool reacts with ozone about twice as fast as does d-limonene (Table 2.8).

Product use rates

Product use rates were determined based on 25 subjects using the spray cleaner and 11 subjects using the disinfectants. In each survey, use rates were reasonably fit by a lognormal distribution, as illustrated in Appendix C, Figures C.1 and C.2. The calculated geometric means (GM) and geometric standard deviations (GSD) of the distributions were 6.0 g m^{-2} and 1.9 for the trigger spray cleaner (GPC-3) and 6.7 g m^{-2} and 2.5 for one of the liquid cleaner and disinfectants (GPC-1). To obtain high but realistic product use rates, we chose levels corresponding to the measured $\text{GM} \times \text{GSD}$, yielding application rates of approximately 11 and 17 g m^{-2} (~ 1 and 1.6 g ft^{-2}) for the trigger spray and liquid cleaner/disinfectant, respectively. Tables C.10 and C.11 in Appendix C provide detailed data for the product use rate experiments. Tables C.12 and C.13 document the details of product masses applied in the simulated cleaning experiments.

Exposure concentrations associated with product use

Selected results for chamber air concentrations measured during product use are presented in Tables 3.29-3.31 and Figures 3.4-3.7. Detailed experimental measurement results are presented in Appendix C, Tables C.14-C.31. Broadly, the results show that concentrations of ethylene-based glycol ethers, terpenes and related unsaturated compounds can reach levels as high as several hundred to several thousand $\mu\text{g m}^{-3}$ under both full-strength and dilute solution use. As displayed in Table 3.31, six unsaturated compounds were measured at time-averaged concentrations in the range 7 to $160 \mu\text{g m}^{-3}$ when the scented-oil air freshener was used. Background concentrations varied but were below $10 \mu\text{g m}^{-3}$ for all but a few cases, such as 2-BE in experiments 1H, 1K, 1O-1P ($14\text{--}20 \mu\text{g m}^{-3}$); and d-limonene in experiment 1P ($33 \mu\text{g m}^{-3}$).

Representative data portraying time-dependent concentration patterns are shown in Figures 3.4-3.7. Concentration profiles for 2-BE varied across applications (Figures 3.4-3.5). Peak concentrations coincided with product use during full-strength counter cleaning with scrub and rinse (Figure 3.4, top). In contrast, peak concentrations were delayed until the second 30-min sampling interval during the dilute-solution floor mopping experiments. The retention of towels in the chamber following counter cleaning led to elevated concentrations during later sampling periods (2-4 h and 4-24 h, top of Figure 3.4). The higher concentrations during the 4-24 h period had a substantial impact on effective emission factors (35-100% increase), as can be seen by comparing experiments 1E-1K with the corresponding experiments 1B-1D (Table 3.30). Figure 3.5 shows that the spray and wipe application (towels retained) resulted in levels of 2-BE that

exceeded $200\ \mu\text{g m}^{-3}$ and $800\ \mu\text{g m}^{-3}$ for 4 h following the cleaning events in experiments 1L and 1M, respectively.

Figure 3.5 includes idealized concentration profiles, which were computed assuming instantaneous emission at the start of cleaning (rather than persistent emissions during and following cleaning) and dynamic behavior of 2-BE corresponding to an inert tracer (e.g., no sorption). For each “idealized” trace, the mass emitted at time $t = 0$ is assumed to match the value calculated for 0-24 h based on the measured concentration profile. The idealized model corresponds closely to the measured profile for experiment 1A, in which GLC-1 was applied full strength and towels were removed from the chamber. Idealized plots differ markedly from profiles measured in experiments 1L and 1M, which included no scrub or rinse steps. The deviations suggest that extended emission of 2-BE occurred over a period of ~ 2 -4 h owing to the continuing presence of used paper towels in the chamber.

Figure 3.6 shows substantial differences in the temporal concentration profiles of the terpene hydrocarbons d-limonene and terpinolene as compared with α -terpineol, a terpene alcohol, with α -terpineol persisting at elevated concentrations 4-24 h after the cleaning event. The left-hand frames in this figure show that retention of towels in the chamber led to higher concentrations notably during the 2-4 h sampling period for the terpenes and throughout the entire experiment for α -terpineol. The lower right-hand frame shows that — as with 2-BE — the peak α -terpineol concentration was delayed until the second 30-min period in the floor-mopping experiment.

The panels on the right side of Figure 3.6 compare measured and idealized profiles for mopping with a dilute solution of GPC-1. The overall behavior of d-limonene and terpinolene is reasonably well predicted by the idealized model, whereas α -terpineol deviates markedly. These observations are consistent with the expectation that, compared with terpene hydrocarbons, terpene alcohols will preferentially remain in aqueous solution or associate with surface-bound water, leading to delayed release.

Sorption of gas-phase analytes to chamber surfaces may also contribute to the persistence of elevated concentrations and to differences between measured and idealized profiles. An initial sorptive uptake rate constant of $0.32\ \text{h}^{-1}$ has been reported for d-limonene in the experimental chamber when furnished (Singer et al., 2004), and values of $1.5 \pm 0.5\ \text{h}^{-1}$ (2-BE) and $2.7 \pm 1.0\ \text{h}^{-1}$ (2-HE) have been determined for glycol ethers in residential bedrooms and bathrooms (Singer et al., 2005). Unpublished experiments indicate that initial adsorption in the chamber in its unfurnished state as used for this study occurs at roughly one-third to one-half of the rate reported for glycol ethers in residential rooms. Thus, sorption was likely competitive with air exchange in the experiments reported herein, and, if so, would have affected the time-dependent concentration profiles.

Concentrations of air-freshener constituents varied over the 3-day experiment as shown in Figure 3.7. For d-limonene, dihydromyrcenol, and linalool, the temporal variability in concentrations correlates reasonably well with the measured changes in overall product volatilization rate. On the other hand, linalyl acetate and especially β -citronellol concentrations increased with time during the first half of the experiment, even though the overall product volatilization rate was declining. This divergence may result from varying volatilization and/or sorption behavior among the constituents.

Owing to the selection of appropriately scaled ratios of cleaned surface to air volume, along with realistic air-exchange and product usage rates, the absolute concentrations observed in the chamber experiments are expected to be relevant to those that would occur in residences,

with the caveat that sorption is likely to play a more significant role in real indoor environments. To illustrate, consider a residence with a floor area of 170 m² (1830 ft²) and volume of 375 m³, typical of US single-family dwellings (Nazaroff and Singer, 2004). In this residence, cleaning of 30 m² of floor or 3.8 m² of hard surfaces – consistent with comprehensive cleaning of kitchen or bathroom surfaces and floors – would achieve the same cleaned surface area to volume ratio as in the present experiments.

The potential for exposures at a level that would raise health concerns also can be evaluated through modeling of cleaning scenarios. Emission factors presented in Tables 3.30-3.31 can be combined with information on product application rate (g m⁻² of cleaned surface), cleaning surface area, mixing volume (i.e., of the room or residence in which the product is used), air-exchange rate, sorption rates and occupancy patterns to estimate inhalation exposure. For example, consider comprehensive cleaning in a 100-m³ efficiency apartment ventilated at 0.5 h⁻¹. Assume that GPC-2 is used to clean 4 m² of hard surfaces and that GPC-3 is used to mop 8 m² of exposed flooring in the kitchen and bath areas. For the purposes of this example, assume initially that sorption of glycol ethers occurs at the same rate as in the experimental room. If the products are applied at the same rate as used in our study, peak 1-h 2-BE concentrations would be ~7 mg m⁻³; if products are applied at twice that rate, 1-h concentrations would reach California's acute REL for 2-BE. Use of products such as these in a closed bathroom, e.g. with a cleaning surface-to-volume ratio that could be an order of magnitude higher than those used in our study, likewise could lead to peak 1-h concentrations near or above the acute REL. Accounting for glycol ether adsorption at rates observed in real residential rooms (Singer et al., 2005) would reduce the estimated 1-h peak concentrations. Nevertheless, these calculations suggest that a more detailed investigation of 2-BE exposure owing to cleaning product use is warranted.

Emissions associated with product use

Emission rates and emission factors associated with product use are presented in Tables 3.29-3.31. These emission factors reflect the mass of each analyte measured in air and thus are relevant for estimating inhalation exposure over a 24-h period for the use of cleaning products and for the initial days of plug-in air freshener use. Emission rates (mg d⁻¹) for individual unsaturated compounds associated with use of AFR-1 are provided in Table 3.29. For the cleaning products, emission factors are presented in Tables 3.30 and 3.31 as mass ratios (mg VOC emitted per g product used); these can be multiplied by product application rate (g m⁻²) and surface area cleaned (m²) to estimate VOC emissions for a cleaning activity.

Figure 3.8 displays fractional emissions of d-limonene and 2-BE associated with various cleaning products and protocols. The emitted fraction varies strongly with application protocol: emission rates were highest for full-strength counter cleaning with towels retained and lowest for mopping with a dilute solution. Full-strength product use that entailed scrubbing and rinsing with a wetted sponge followed by wiping with paper towels produced fractional emissions in the range ~50-70% when towels were retained in the chamber (experiments 1E-1K) and ~25-50% when towels were removed. The difference between these two groups of experiments is consistent with the expectation that some of the volatile constituents were retained in the water used during scrub and rinse procedures, and some was bound in the paper towels used in clean-up. In experiments 1L and 1M, computed fractional emissions of 2-BE were very high, exceeding 100% based on the mean composition values. Note that there is significant uncertainty in the 2-BE composition of individual cleaning products (see Table 3.27).

The low fractional emissions associated with mopping (2% for 2-BE and 7-11% for d-limonene) are not unexpected, since most of the cleaning solution remained in the bucket and was removed from the chamber at the conclusion of cleaning. About 8-10% of the solution was applied to the floor during the wet mop stage and about 2-3% remained in the chamber after dry mopping. These data suggest that during the wet mop stage, when excess cleaning solution was applied to the floor, a substantial fraction of the d-limonene in that solution volatilized before the solution was collected during the dry mop stage. In contrast, the ~2% fractional emissions of 2-BE are consistent with the net amount of solution dispensed, suggesting little volatilization from the excess solution applied during the wet mop stage.

Fractional emissions of terpenes and terpene alcohols from GPC-1 are presented in Figure 3.9. Consistent with results for other products, the emitted fraction of dispensed product was highest for full-strength product use with towel retention, lower for full-strength use with towel removal, and lowest for the dilute floor-mopping application. In addition to this dependence on application method, a dichotomy is apparent between the terpene hydrocarbons and terpene alcohols. In the floor-mopping scenario, fractional emissions of terpene alcohols were in the range of 2-5% whereas terpene emissions were in the range of 7-12%. The discrepancy was even larger for full-strength counter cleaning: 2-9% for the alcohols versus 20-50% for the terpenes with towel removal, and 7-30% for the alcohols versus 35-70% for the terpenes with paper towels retained. Factors likely influencing these results include slower volatilization of the alcohols during initial application and greater partitioning of alcohols into the water during scrub and rinse procedures.

Experimental uncertainty, variability, and bias

Several sources of uncertainty, variability and bias associated with the experimental results were assessed. Uncertainty associated with the quantitation of individual VOC concentrations during a sampling interval was evaluated by analysis of results from duplicate samples, including $n = 28$ pairs for 2-BE, $n = 5$ for 2-HE, $n = 15$ for d-limonene, $n = 7$ for terpenes and terpene alcohols in GPC-1 and $n = 2$ for unsaturated compounds specific to AFR-1. Mean relative deviations were generally less than 5-8%, excepting α -terpinene (22%), terpinolene (16%), γ -terpineol (17%), and α -phellandrene (13%). Imprecision in the amount of product used was ± 0.1 g. Replicate counter-cleaning experiments with GPC-3 (1F-1H, Table 3.30) and GPC-4 (1I-1K, Table 3.30) informs variability associated with implementation of experimental protocols, and indicates good precision. Variability in the product composition measurements is presented in Tables 3.29. Variability in air-exchange rate during the course of an experiment was determined to be $< 5\%$ based on successive tracer-decay measurements. The effect of sorption and desorption processes represents another source of uncertainty and potential bias. Some emitted product constituents, including glycol ethers and terpene alcohols, likely sorbed during experiments. Any product constituent that remained sorbed to chamber material surfaces at the end of the 24 h experiment is not included in the calculated emission factors. Uncertainty in calculated emission factors associated with longer-term desorption was estimated to be ~2% for experiments 1L and 1P and much less for other experiments.

3.5. Study Implications of Evolving California Consumer Product Regulations

Volatile organic compounds contribute to photochemical smog in ambient air. A large proportion of California, including its most populous air basins, is classified as “nonattainment” with regard to ambient ozone. A consequence of this classification is the need to develop state

implementation plans to reduce the emissions of reactive precursors, including VOCs, so as to make progress toward the regulatory standard. As one of many measures developed for this purpose, California has adopted regulations that limit photochemically reactive VOC content of consumer products, including cleaning products. The cleaning products characterized in this project come under the “consumer products regulation,” which was first adopted in 1990 and has been amended several times since. All of the products tested here, except disinfectants and multipurpose solvents, are subject to the VOC content limits, as shown in Table 3.32. Subsequent to the selection of products for this project, more stringent VOC limits became effective for several of the product types, including non-aerosol general purpose cleaners, general purpose degreasers, and furniture maintenance products. We do not know whether the products currently sold have the same composition as the products tested.

3.6. Conclusions

Common cleaning products marketed to consumers may contain terpenes, terpene alcohols, or ethylene-based glycol ethers at low percent levels. Application of the products at rates relevant to a comprehensive residential cleaning event can lead to 1-h peak concentrations on the order of tenths to several mg m^{-3} . When the products are used in full-strength, hard-surface cleaning applications, substantial percentages of the dispensed active ingredients are volatilized. The amount volatilized depends on the application protocol, allowing opportunities for exposure mitigation. For example, a substantial fraction of the volatile ingredients may be temporarily captured in towels used to wipe the product from a surface; prompt removal of used cleaning materials thus may reduce exposure. When applied in dilute solution, e.g. as occurs in floor mopping, larger quantities of product are dispensed, but lower fractions of the active ingredients are volatilized. The fraction volatilized during dilute application varies by chemical class; terpenes such as d-limonene volatilize from solution more readily than the hydrophilic glycol ethers and terpene alcohols. In many experiments, the temporal profile of measured concentrations deviated from the idealized pattern that would be expected if the active ingredients were volatilized instantaneously when the product was used and were removed only by air exchange. The deviations result from delayed emissions, for example owing to preferential partitioning of polar constituents in liquid water, and potentially to sorption phenomena. These processes reduce peak concentrations but lead to elevated levels in air for several hours or more after a cleaning event.

The work described in this section contributes to efforts to better understand human exposures to primary and secondary pollutants associated with cleaning product use. Results provide information that is directly relevant to emissions and resulting gas-phase concentrations of ethylene-based glycol ethers (primary pollutants) and terpenoids that react with ozone to form secondary pollutants. Simplified modeling of cleaning scenarios using the emission factors determined in this study indicates that peak 1-h exposure concentrations for 2-butoxyethanol might approach or potentially exceed California’s acute reference exposure level of 14 mg m^{-3} in some situations. d-Limonene and other ozone-reactive terpenoids present in cleaning products can reach mg m^{-3} levels in air and persist at levels of tens to hundreds of $\mu\text{g m}^{-3}$ for many hours after cleaning. Air fresheners can produce steady-state levels of tens to hundreds of $\mu\text{g m}^{-3}$ of ozone-reactive terpenoids. Use of cleaning products and air fresheners in the presence of elevated indoor ozone is of concern because of the formation of secondary air pollutants that pose health risks.

Table 3.33 provides a concise summary of the specific findings reported in §3.

Table 3.1. Number of retail outlets in California's 15 largest cities for ten major corporations selling consumer products.

City	Population	Number of Retail Outlets									
		Safeway / Vons	Albertsons	Longs Drugs	Smart&Final	Wal-Mat	Target	Costco	Home Depot	ACE Hardware	OSH
Los Angeles	3,800,000	26	15	6	14	1	4	1	8	7	3
San Diego	1,260,000	42	21	10	6	4	6	4	9	11	1
San Jose	900,000	20	19	15	3	1	5	2	5	2	7
San Francisco	760,000	15	4	0	4	0	0	1	0	11	1
Long Beach	470,000	4	10	0	3	2	5	1	3	5	2
Fresno	450,000	6	4	8	3	3	3	2	3	2	2
Sacramento	440,000	6	11	10	5	5	3	2	5	3	2
Oakland	400,000	6	7	9	2	0	0	1	2	5	0
Santa Ana	340,000	2	5	1	3	1	1	1	2	1	1
Anaheim	330,000	2	3	0	1	1	2	0	3	1	0
Riverside	270,000	1	4	1	2	2	3	0	1	4	0
Bakersfield	260,000	8	7	5	3	2	2	2	3	2	1
Stockton	260,000	1	0	3	1	1	1	1	2	3	1
Fremont	210,000	4	6	3	1	0	1	1	1	2	1
Modesto	200,000	2	0	4	2	1	2	1	1	1	1
Total No. Outlets		145	116	75	53	24	38	20	48	60	23

Table 3.2. Locations of five surveyed retail stores

Store Name	Parent Company	Address
Safeway	Safeway Inc.	Shattuck Place, Berkeley, CA 94709
Longs Drugs	Longs Drug Stores Corp.	Shattuck Avenue, Berkeley, CA 94709
Smart&Final	Smart & Final, Inc.	Broadway, Oakland, CA 94607
Wal-Mart	Wal-Mart	Davis Street, San Leandro, CA 94577
Home Depot	Home Depot, Inc.	Hollis Avenue, Emeryville, CA 94608

Table 3.3. ARB consumer product categories surveyed

ARB Consumer Product Category	Assigned Category Code	Appendix Table ^a
Disinfectant	DIS	A.1
General purpose degreaser	GPD	A.2
Multi-purpose solvent	MPS	A.2
General purpose cleaner	GPC	A.3
Glass cleaner	GLC	A.4
Dusting aid	DST	A.5
Furniture maintenance product	FMP	A.5
Wood Cleaner	WDC	A.5
Carpet & upholstery cleaner	CUC	A.6
Spot remover	SRM	A.6
Floor polish or wax	FPW	A.7
Floor wax stripper	FWS	A.7
Bathroom & tile cleaner	BTC	A.8
Metal polish/Cleanser	MTL	A.8
Oven cleaner	OVN	A.8
Air freshener ^b	AFR	A.9

^a Appendix A table containing shelf survey results for category

^b Includes dual purpose air freshener/disinfectants

Table 3.4. Number of consumer products and represented manufacturers by category at each store surveyed.

Product Category	No. Manufacturers by Category	Total No. Products by Category	Number of Products				
			Safeway	Longs Drugs	Smart&Final	Wal-Mart	Home Depot
Disinfectants	5	21	3	4	13	7	3
General purpose degreasers, Multi-purpose solvents	9	16	0	0	11	6	2
General purpose cleaners	16	72	23	15	32	26	15
Glass cleaners	7	21	6	6	11	9	5
Dusting aids, Furniture maintenance products, Wood cleaners	7	26	15	3	9	13	5
Carpet & upholstery cleaners, Spot removers	9	24	10	4	12	6	4
Floor polishes/waxes, Floor wax strippers	3	8	6	6	11	9	5
Bathroom & tile cleaners, Metal polish/cleaners, Oven cleaners	6	14	2	2	12	4	2
Air fresheners	13	89	41	12	13	55	3
Total No. Products		291	101	46	120	127	39

Table 3.5. Number of consumer products by category for 18 manufacturers with three or more products in shelf survey

Manufacturer	Total	Number of Products ^a								
		DIS	GPD + MPS	GPC	GLC	DST + FMP + WDC	CUC + SRM	FPW + FWS	BTC + MTL + OVN	AFR
Acuity Specialty Prod. Grp.	22			11	3	2	3			3
Big D Industries, Inc.	5									5
Carroll Company	7		4			1			2	
Church & Dwight Co, Inc.	4									4
Colgate-Palmolive Co.	7	7		6	1					
Dial Corp.	7									7
JohnsonDiversey	4					4				
North American Oil Co.	4			1						3
Orange Glo International	7		3	2		2				
Procter & Gamble	5			5						
Reckitt Benckiser	63	11	1	14		3	8	3	5	18
Sara Lee Corp.	3									3
SC Johnson	68			5	12	12				39
Scott's Liquid Gold, Inc.	5					2				3
Smart & Final, Inc.	21	4	2	3	1		4	4	3	
Sunshine Makers, Inc.	3			3						
The Clorox Company	23	4	2	12	2		3			
White Cap, Inc.	4			4						

^a Product category codes are defined in Table 3.3

Table 3.6. Summary information for 50 products selected from shelf survey as potential candidates for further study

Product Category	Category Code	No. of Products	No. of Manufact.	No. with MSDS	No. with Label Info.
Disinfectant	DIS	6	2	2	—
General purpose degreaser	GPD	3	2	2	1
General purpose cleaner	GPC	19	10	10	4
Glass cleaner	GLC	4	2	3	—
Wood Cleaner	WDC	5	4	1	—
Carpet & upholstery cleaner	CUC	2	2	1	—
Air freshener	AFR	11	4	*	

*All air fresheners assumed to contain compounds of interest

Table 3.7. Consumer products investigated in experiments performed during this research. ^a

Product Code	Consumer Product Category	Product Form	Composition Data Tables ^b	P ^c	S ^c
DIS-1	Disinfectant	Trigger spray	3.13, 3.20, B.3		
GPD-1	General purpose degreaser	Aerosol spray	3.11, 3.16, 3.18, B.1		✓
GPC-1	General purpose cleaner	Liquid	3.9, 3.12, 3.16, 3.19, 3.27, 3.28, B.2, C.7, C.8	✓	✓
GPC-2	General purpose cleaner	Trigger spray	3.13, 3.18, 3.27, B.3, C.4	✓	
GPC-3	General purpose cleaner	Trigger spray	3.13, 3.20, 3.27, B.4, C.5	✓	
GPC-4	General purpose cleaner	Trigger Spray	3.11, 3.13, 3.16, 3.18, 3.19, 3.27, B.1, B.4, C.6	✓	
GPC-5	General purpose cleaner	Trigger spray	3.14, B.6		
GPC-6	General purpose cleaner	Liquid	3.12, 3.16, B.2		
GPC-7	General purpose cleaner	Liquid	3.12, 3.16, B.2		
GLC-1	Glass cleaner	Trigger spray	3.10, 3.13, 3.18, 3.20, 3.27, B.5, C.3	✓	
WDC-1	Wood cleaner	Liquid	3.14, B.6		
FMP-1	Furniture maintenance product	Trigger spray	3.11, 3.16, 3.18, B.1		
FMP-2	Furniture maintenance product	Liquid	3.14, B.6		
FMP-3	Furniture maintenance product	Aerosol spray	3.14, 3.16, B.6		
FMP-4	Furniture maintenance product	Aerosol spray	3.14, 3.16, B.6		
SRM-1	Spot remover	Aerosol spray	3.13, 3.18, B.4		
MPS-1	Multi-purpose solvent	Liquid	3.11, 3.16, B.1		
AFR-1	Air freshener	Oily liquid, Plug in	3.15, 3.16, 3.29, B.7, C.9	✓	✓
AFR-2	Air freshener	Oily liquid, Plug in	3.15, 3.16, B.7		
AFR-3	Air freshener	Gel, Plug in	3.15, 3.16, B.7		
AFR-4	Air freshener	Aerosol spray	3.15, B.7		

^a Products are identified by code numbers^b Tables presenting results for mass fractions of target VOCs contained in product.^c “✓” indicates that experiments were conducted to determine concentrations and emissions for primary constituents (P; see §3.4) or for secondary pollutants (S; see §4) involving reactions with ozone.

Table 3.8. Target compounds. ^a

Target Compounds by Class	CAS No.	RT (min)	FW ^b	Reaction w/ O ₃ k (ppb ⁻¹ s ⁻¹)
<i>Terpene Hydrocarbons</i>				
α-Pinene	80-56-8	22.4	136.2	2.1 × 10 ⁻⁶ (a) ^c
Camphene	79-92-5	23.3	136.2	2.2 × 10 ⁻⁸ (b)
β-Pinene	127-91-3	24.5	136.2	3.7 × 10 ⁻⁷ (a)
β-Myrcene ^{d,e}	123-35-3	25.0	136.2	1.2 × 10 ⁻⁵ (a)
3-Carene	13466-78-9	25.6	136.2	9.3 × 10 ⁻⁷ (a)
α-Phellandrene ^d	99-83-2	25.7	136.2	7.4 × 10 ⁻⁵ (c)
α-Terpinene	99-86-5	26.1	136.2	5.2 × 10 ⁻⁴ (c)
d-Limonene	5989-27-5	26.4	136.2	5.2 × 10 ⁻⁶ (a)
γ-Terpinene	99-85-4	27.5	136.2	3.4 × 10 ⁻⁶ (a)
Terpinolene	586-62-9	28.5	136.2	4.7 × 10 ⁻⁵ (c)
<i>Unsaturated Oxygenated Compounds</i>				
Dihydromyrcenol ^{d,e}	18479-58-8	30.1	156.3	
Linalool	78-70-6	31.0	154.2	1.1 × 10 ⁻⁵ (d)
1-Terpineol ^d	586-82-3	32.3	154.2	
β-Terpineol ^d	138-87-4	33.2	154.2	
4-Terpineol ^d	562-74-3	33.6	154.2	
Terpineol isomer ^d		34.0	154.2	
α-Terpineol	98-55-5	34.6	154.2	7.4 × 10 ⁻⁶ (e)
γ-Terpineol ^{d,e}	586-81-2	34.7	154.2	
Linalyl acetate ^{d,e}	115-95-7	35.0	196.3	
β-Citronellol	1117-61-9	35.6	156.3	
cis-Citral ^{d,e}	106-26-3	36.6	152.2	
trans-Citral ^{d,e}	141-27-5	37.5	152.2	
<i>Ethylene-Based Glycol Ethers</i>				
2-Butoxyethanol	111-76-2	24.5	118.2	
2-Hexyloxyethanol	112-25-4	31.6	146.2	
<i>Other compounds</i>				
Xylenes (o-, m-, & p-isomers)	1330-20-7	21.3-22.4	106.2	

^a Terpene hydrocarbons, unsaturated oxygenated compounds and ethylene-based glycol ethers present in the vapor phase of consumer products analyzed by bag method. Compounds are ordered by increasing chromatographic retention time (RT) within each chemical class. Reported 2nd order rate constants for reactions of selected compounds with ozone are shown. See notes regarding identification and quantitation of compounds.

^b Formula weight (= molecular mass), in units of g/mol.

^c References: (a) = Atkinson, et al. (1990b); (b) = Atkinson, et al., (1990a); (c) = Shu and Atkinson (1994); (d) = Atkinson, et al. (1995); (e) = Wells (2005).

^d Identification based on match to electronic library; quantified using d-limonene total-ion-current response factor.

^e Identification subsequently confirmed by analysis of pure compound.

Table 3.9. Mass fractions of ozone-reactive VOCs in three containers (A, B and C) of general purpose cleaner GPC-1 determined by bag method. ^a

Compound	Mass Fraction of Compound in Product (%)					
	A1	A2	B	C1	C2	$\mu \pm \sigma$ ^b
α -Pinene	0.18	0.17	0.33	0.19	0.23	0.24 ± 0.08
Camphene	0.10	0.10	0.12	0.09	0.11	0.11 ± 0.01
β -Pinene	0.03	0.03	0.07		0.06	0.05 ± 0.02
α -Phellandrene ^c	0.04	0.03	0.03	0.04	0.03	0.03 ± 0.00
α -Terpinene	0.17	0.16	0.12	0.15	0.10	0.14 ± 0.02
d-Limonene	1.14	1.12	1.07	1.10	1.06	1.09 ± 0.03
γ -Terpinene	0.14	0.14	0.12	0.17	0.14	0.14 ± 0.02
Terpinolene	1.66	1.62	1.73	1.89	1.24	1.65 ± 0.08
1-Terpineol ^c	0.42	0.36	0.36	0.42	0.45	0.40 ± 0.04
β -Terpineol ^c	0.17	0.15	0.15	0.15	0.18	0.16 ± 0.01
4-Terpineol ^c	0.08	0.08	0.07	0.10	0.09	0.08 ± 0.01
Terpineol isomer ^c	0.06	0.09	0.05	0.05	0.06	0.06 ± 0.01
α -Terpineol	2.8	3.4	2.8	3.2	2.8	3.0 ± 0.13
γ -Terpineol ^c	0.45	0.56	0.43	0.50	0.42	0.47 ± 0.04

^a Containers A and C were analyzed in duplicate

^b Average and standard deviation for three containers

^c Quantified using d-limonene total-ion-current response factor

Table 3.10. Mass fractions of ethylene-based glycol ethers in three containers (A, B and C) of glass cleaner GLC-1 determined by bag method. ^a

	Mass Fraction of Compound in Product (%)						
Compound	A1	A2	B1	B2	C1	C2	$\mu \pm \sigma$ ^b
2-Butoxyethanol	0.60	0.60	0.56	0.57	0.61	0.61	0.59 ± 0.02
2-Hexyloxyethanol	0.19	0.24	0.25	0.25	0.27	0.25	0.24 ± 0.02

^a All containers were analyzed in duplicate

^b Average and standard deviation for three containers

Table 3.11. Mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers determined by bag method analysis of four cleaning products with >3% d-limonene.

Compound	Mass Fraction of Compound in Product (%)			
	GPD-1	GPC-4 ^a	FMP-1	MPS-1
α -Pinene	0.20 ^b	0.03	0.05	0.11
β -Pinene		0.02	0.03	0.08
β -Myrcene ^c	0.43 ^b	0.07	0.10	0.22
d-Limonene	25	3.9	5.4	10.2
2-Butoxyethanol		1.7		

^a Values are averages for three bags

^b Relative deviation >50%; compounds were present only in sample with five-fold higher injection volume

^c Quantified using d-limonene total-ion-current response factor

Table 3.12. Mass fractions of ozone-reactive VOCs determined by bag method analysis of three cleaning products with pine oil constituents. ^a

Compound	Mass Fraction of Compound in Product (%)				
	GPC-1 A	GPC-1 B ^b	GPC-1 C	GPC-6	GPC-7
α -Pinene	0.18	0.33	0.21	0.05	0.10
Camphene	0.10	0.12	0.10	0.01	0.03
β -Pinene	0.03	0.07	0.06 ^c	0.01	0.02
α -Phellandrene ^d	0.04	0.03	0.04		0.01
α -Terpinene	0.17	0.12	0.13	0.01	0.08
d-Limonene	1.13	1.07	1.06	0.22	0.38
γ -Terpinene	0.14	0.12	0.16	0.01	0.06
Terpinolene	1.64	1.73	1.57	0.04	0.42
1-Terpineol ^d	0.39	0.36	0.44	0.01	0.13
β -Terpineol ^d	0.16	0.15	0.17		0.07
4-Terpineol ^d	0.08	0.07	0.10		0.13
Terpineol isomer ^d	0.08	0.05	0.06		0.09
α -Terpineol	3.1	2.8	3.0	0.01	0.69
γ -Terpineol ^d	0.51	0.43	0.46		0.10

^a Results for three individual containers are shown for GPC-1

^b Analysis of single bag

^c Relative deviation >50%

^d Quantified using d-limonene total-ion-current response factor

Table 3.13. Mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers determined by bag method analysis of six cleaning products with >0.5% 2-butoxyethanol. ^a

Compound	Mass Fraction of Compound in Product (%)							
	DIS-1	GPC-2	GPC-3	GPC-4 ^b	GLC-1 A	GLC-1 B	GLC-1 C	SRM-1
α -Pinene				0.03				
β -Pinene				0.02				
β -Myrcene ^c				0.07				
d-Limonene				3.9				
2-Butoxyethanol	4.7 ^d	2.6	4.2	1.7	0.60	0.57	0.61	9.6 ^d
2-Hexyloxyethanol					0.22	0.25	0.26	

^a Results for three individual containers are shown for GLC-1

^b Values are averages for three bags

^c Quantified using d-limonene total-ion-current response factor

^d Relative deviation >50%

Table 3.14. Mass fractions of ozone-reactive VOCs and xylenes determined by bag method analysis of five cleaning products with <0.2% of individual target compounds.

Compound	Mass Fraction of Compound in Product (%)				
	GPC-5	WDC-1	FMP-2	FMP-3	FMP-4
α -Pinene				0.01	0.01 ^b
β -Pinene				0.04	
β -Myrcene ^a					0.03
d-Limonene		0.01 ^b		0.19	0.14
γ -Terpinene				0.01	0.01
Dihydromyrcenol ^a	0.01				
<i>cis</i> -Citral ^a				0.01	0.01
<i>trans</i> -Citral ^a				0.02	0.02
Xylenes			0.07		

^a Quantified using d-limonene total-ion-current response factor

^b Relative deviation >50%

Table 3.15. Mass fractions of ozone-reactive VOCs determined by bag method analysis of four air-freshener products.^a

Compound	Mass Fraction of Compound in Product (%)			
	AFR-1	AFR-2	AFR-3	AFR-4
α -Pinene		0.12		
Camphene	0.04 ^b			
β -Pinene	0.12	0.14		
β -Myrcene ^c	0.10 ^b	0.08		
3-Carene		0.03 ^b		
α -Terpinene				
d-Limonene	1.26	1.18	0.94 ^b	0.02
γ -Terpinene		0.12		
Terpinolene		0.03		
Dihydromyrcenol	5.0		3.5 ^b	
Linalool	4.0	8.8	4.8 ^b	0.01
β -Terpineol ^c		0.09		
α -Terpineol		0.34		
γ -Terpineol ^c		0.12		
Linalyl acetate ^c	2.3	2.9		
β -Citronellol	0.65			
<i>cis</i> -Citral ^c				0.01
<i>trans</i> -Citral ^c				0.01

^a Three products had $\geq 4\%$ linalool

^b Relative deviation > 50%

^c Quantified using d-limonene total-ion-current response factor

Table 3.16. Mass fractions of d-limonene and total ozone-reactive VOCs determined by bag method analysis of consumer products

Consumer Products by Category	Mass Fraction of Compound in Product (%)	
	d-Limonene	Ozone-reactive VOCs ^a
<i>General Purpose Degreaser</i>		
GPD-1	25	26
<i>General Purpose Cleaners</i>		
GPC-1	1.09	7.6
GPC-4	3.8	3.9
GPC-6	0.22	0.37
GPC-7	0.38	2.3
<i>Furniture Maintenance Products</i>		
FMP-1	5.4	5.6
FMP-3	0.19	0.28
FMP-4	0.14	0.22
<i>Multi-Purpose Solvent</i>		
MPS-1	10.2	10.6
<i>Air Fresheners</i>		
AFR-1	1.26	13.5
AFR-2	1.18	14.0
AFR-3	0.94	9.2

^a Includes all terpene hydrocarbons and unsaturated oxygenated compounds listed in Table 3.8

Table 3.17. Additional abundant compounds detected by bag method analysis of consumer products

Consumer Product/ Compound	Consumer Product/ Compound	Consumer Product/ Compound
<i>GPC-1</i> 2-Propanol	<i>FMP-3</i> C ₇ -C ₈ Branched alkane HCs ^{a,b} Octamethylcyclotetrasiloxane Unident. siloxane compound	<i>AFR-2</i> Eucalyptol Di(propylene glycol) butyl ethers Camphor Isobornyl acetate Tri(propylene glycol) methyl ethers
<i>GPC-4</i> Di(propylene glycol) butyl ethers	<i>FMP-4</i> C ₈ Branched alkane HC ^b Octamethylcyclotetrasiloxane Unident. siloxane cmpds (2)	
<i>GPC-5</i> Di(propylene glycol) butyl ethers	<i>MPS-1</i> n-Decane n-Undecane n-Dodecane n-Tridecane C ₁₁ -C ₁₃ Cyclic & aliphatic HCs ^b	<i>AFR-3</i> Acetic acid, isononyl ester ^b Benzyl acetate 4- <i>cis</i> -Butylcyclohexyl acetate ^b 4- <i>tert</i> -Butylcyclohexyl acetate ^b
<i>GPC-7</i> 2-Propanol		<i>AFR-4</i> Butylated hydroxytoluene Unident.compound
<i>GLC-1</i> 2-Propanol		
<i>FMP-1</i> C ₁₃ -C ₁₅ Branched alkane HCs ^b	<i>AFR-1</i> Acetic acid, isononyl ester ^b Isobornyl acetate α,α -Dimethylbenzene ethanol acetate ^b Unident. compound	
<i>FMP-2</i> C ₈ -C ₉ Cyclic & aliphatic HCs ^b Benzaldehyde		

^a HCs = hydrocarbons

^b Identification based on match to electronic library

Table 3.18. Comparison of product mass fraction formulations of d-limonene and 2-butoxyethanol as reported by manufacturers in Material Safety Data Sheets with mass fractions determined by bag method analysis of six cleaning products

Cleaning Product	d-Limonene (%)		2-Butoxyethanol (%)	
	MSDS	Analysis	MSDS	Analysis
GPD-1	20 ^a	25		
GPC-2			0.5-5	2.6
GPC-4	<5	3.8	<5	1.68
GLC-1			0.5-1.5	0.59
FMP-1	<10 ^a	5.4		
SRM-1	NL ^b	0.07	<25	9.6

^a Listed as orange oil in MSDS; orange oil contains ~ 90% d-limonene

^b NL = Not listed

Table 3.19. Comparison of mass fractions of ozone-reactive VOCs and ethylene-based glycol ethers in general-purpose cleaners GPC-1 and GPC-4 determined by direct analysis of products diluted in methanol and by bag method analysis of vapor-phase

Target Compounds by Class	Mass Fraction of Compound in Product (%)			
	GPC-1		GPC-4	
	Sol. Dil.	Bag Mth.	Sol. Dil.	Bag Mth.
<i>Terpene Hydrocarbons</i>				
α -Pinene	0.2	0.24	+ ^a	0.03
Camphene	0.1	0.11		
β -Pinene		0.05	0.2	0.02
β -Myrcene ^b				0.07
3-Carene		0.03		
α -Terpinene	0.2	0.14		
d-Limonene	1.3	1.09	4.0	3.8
γ -Terpinene	0.2	0.14		
Terpinolene	1.9	1.65		
<i>Terpene Alcohols</i>				
1-Terpineol ^b	0.9	0.40		
β -Terpineol ^b	0.5	0.16		
4-Terpineol ^b	0.4	0.08		
Terpineol isomer ^b	0.2	0.06		
α -Terpineol	5.6	3.0		
γ -Terpineol ^b	1.1	0.47		
<i>Ethylene-based Glycol Ether</i>				
2-Butoxyethanol			2.4	1.68

^a + = present but not quantified

^b Quantified using d-limonene total-ion-current response factor

Table 3.20. Comparison of mass fractions of ethylene-based glycol ethers in cleaning products DIS-1, GPC-3, and GLC-1 determined by direct analysis of products diluted in methanol and by bag method analysis of vapor-phase

Ethylene-based Glycol Ethers	Mass Fraction of Compound in Product (%)					
	DIS-1		GPC-3		GLC-1	
	Sol. Dil.	Bag Mth.	Sol. Dil.	Bag Mth.	Sol. Dil.	Bag Mth.
2-Butoxyethanol	5.6	4.7	4.3	4.2	0.7	0.59±0.02
2-Hexyloxyethanol					0.4	0.24±0.02

Table 3.21. Applications considered for a disinfectant and other cleaning products. ^a

Cleaning Product	Product Applications During House Cleaning
<i>Disinfectant</i>	
DIS-1	Basins, toilets, tubs, showers, sink, kitchen appliances, hood, resilient & tile floors (commercial product)
<i>General Purpose Degreaser</i>	
GPD-1	Kitchen appliances, oven & range hood
<i>General Purpose Cleaners</i>	
GPC-1	Basins, toilets, tubs, showers, sink, kitchen appliances, counters, resilient & tile floors
GPC-2	Basins, toilets, tubs, showers, sink, kitchen appliances, counters
GPC-3	Basins, toilets, tubs, showers, sink, kit. appliances, oven & range hood, counters, cabinets, resilient & tile floors
GPC-4	Basins, toilets, tubs, showers, sink, kit. appliances, oven & range hood, counters, cabinets, resilient & tile floors
GPC-5	Kitchen appliances, sink, kitchen counters
GPC-6	Basins, toilets, tubs, showers, sink, kitchen appliances, counters, resilient & tile floors
GPC-7	Basins, toilets, tubs, showers, sink, kitchen appliances, counters, resilient & tile floors
<i>Glass Cleaner</i>	
GLC-1	Windows & mirrors, tubs, showers, kitchen appliances, counters
<i>Wood Cleaner</i>	
WDC-1	Wood floors, cabinets & paneling
<i>Furniture Maintenance Products</i>	
FMP-1	Cabinets & paneling, wood furniture
FMP-2	Cabinets & paneling, wood furniture
FMP-3	Cabinets & paneling, wood furniture
FMP-4	Cabinets & paneling, wood furniture
<i>Spot Remover</i>	
SRM-1	Carpet & upholstery (stain removal, occasional use)
<i>Multi-Purpose Solvent</i>	
MPS-1	Resilient floor wax removal (infrequent use)

^a All applications are assumed to occur during routine house cleaning unless indicated.

Table 3.22. Dilution factors interpreted from information on manufacturers’ product labels for various cleaning applications of a disinfectant and five general-purpose cleaners.

Cleaning Task	Manufacturer Recommended Dilution Factors					
	DIS-1 ^a	GPC-1	GPC-3 ^a	GPC-4 ^a	GPC-6	GPC-7
Kitchen appliances	FS ^b	1/64	1/10	1/2	1/64	1/32
Oven & range hood	FS	FS	FS	1/2	FS	FS
Kitchen sink	FS	1/64	1/10	1/2	1/64	1/32
Kitchen counters	FS	1/64	1/10	1/2	1/64	1/32
Bathroom basins & toilets	FS	FS	1/10	1/2	FS	FS
Bathroom tubs & showers	FS	1/64	1/10	1/2	1/64	1/32
Bathroom counters	FS	1/64	1/10	1/2	1/64	1/32
Cabinets & paneling			1/30	1/20		
Floors, non-wood	1/16	1/64	1/30	1/20	1/64	1/32

^a Packaged in trigger spray bottle

^b FS = Full strength use

Table 3.23. Cleaning tasks and cleaning surface areas estimated to be typical for a 140-m², three-bedroom, two-bath house

Cleaning Task	Surface Area (m²)
Kitchen appliances	2.5
Oven & range hood	1.3
Kitchen sink	0.6
Kitchen counters	5
Bathroom basins & toilets	1
Bathroom tubs & showers	10
Bathroom counters	3.4
Cabinets & paneling	9
Windows & mirrors	17
Carpet & upholstery	20 ^a
Hard floors (not wood)	8 ^b
Wood furniture	20

^a Total carpeted floor area is approximately 105 m²

^b Total non-carpeted floor area is approximately 35 m²

Table 3.24. Estimated consumer product use rates (g/use) and potential emissions (g/use) of ozone-reactive VOCs and ethylene-based glycol ethers for cleaning products and plug-in air fresheners. ^a

		Potential Emissions (g/use)		
Consumer Products by Category	Prod. Use Rate ^b (g/use)	Ozone-reactive VOCs	Ethylene-based Glycol Ethers	Assumed Frequency of Use ^c
Disinfectant				
DIS-1	245		11.5	D, W
General Purpose Degreasers				
GPD-1	25	6.5		W
General Purpose Cleaners				
GPC-1	30	2.3		D, W
GPC-2	225	17.1	5.8	D, W
GPC-3	40 (330)		1.7 (13.9)	D, W
GPC-4	130 (330)	5.1 (12.9)	2.2 (5.5)	D, W
GPC-6	30	0.11		D, W
GPC-7	30	0.69		D, W
Glass Cleaner				
GLC-1	380		3.2	D, W
Furniture Maintenance Products				
FMP-1	290	16.2		W
FMP-3	175	0.49		W
FMP-4	175	0.39		W
Spot Remover				
SRM-1	120		11.5	O
Multi-Purpose Solvent				
MPS-1	80	8.5		O
Air Fresheners				
AFR-1	5 ^d	0.68 ^d		Co
AFR-2	5 ^d	0.70 ^d		Co
AFR-3	1.2 ^d	0.12 ^d		Co

^a Products GPC-3 and GPC-4 with recommended dilutions but packaged in trigger spray bottles were evaluated for recommended use and all full strength use (FS in parentheses). Three cleaning products and one aerosol air freshener lacking substantial content of target VOCs (GPC-5, WDC-1, FMP-2, and AFR-4) are omitted

^b Products packaged in trigger spray bottles are assumed to be used in dilute form for floor cleaning and full strength for other applications

^c D = Daily or potentially daily, but not for all applications; W = weekly or bi-weekly cleaning; O = occasional or infrequent use; Co = Continuous use

^d Assumed constant emission rate; use period is one week; rate is g/week.

Table 3.25. Summary information for six products employed in simulated-use experiments.

Product	Constituents of interest	Package form	Recommended uses (selected from packaging), directions, and dilutions in water. ^a
GLC-1	2-butoxyethanol, 2-hexyloxyethanol	trigger spray	Glass, plastic, enamel, tile, porcelain; appliances, stovetops, counters, cabinets, vanities, windows. Spray directly onto surface, wipe dry with towel.
GPC-1	terpenes, terpene alcohols (pine oil)	capped bottle	Hard, non-porous household surfaces (counters, sinks, stoves, showers, tile, floors, toilet, etc.). 1/4 cup/gal: general cleaning. FS for tough jobs. Disinfection: wipe FS onto surface, let stand 5 min, remove excess.
GPC-2	2-butoxyethanol	trigger spray	Kitchen grease, bathroom soils, household. Spray straight onto soils, wipe clean with a dry paper towel or cloth. Repeat for heavily soiled areas.
GPC-3	2-butoxyethanol	trigger spray	FS: Ovens, grills, range hoods, vents, etc. 1:10: Counters, stove-tops, refrigerators, sinks, showers, tubs, tile, toilets, etc. 1:30: Floors (vinyl, tile, wood), painted surfaces, chrome, plastic, cabinets, blinds, carpets/fabrics.
GPC-4	2-butoxyethanol, d-limonene	trigger spray	1:1: Appliances, countertops, sinks, ovens, basins, tubs, showers, aluminum, ceramic tile. 1:20: Cabinets, walls, floors & painted surfaces.
AFR-1	unsaturated terpenoids (scented oil)	plug-in heated dispenser	Dispenser volatilizes product constituents over several weeks

^a FS = full strength

Table 3.26. Summary of 18 simulated-use experiments conducted in 50-m³ chamber.

Product	Expt	Start date (2003)	Product used (g)	AER ^a (h ⁻¹)	T (°C) $\mu \pm \sigma$	RH (%) $\mu \pm \sigma$
<i>Counter cleaning with scrub and rinse, full strength product; towels removed</i>						
GLC-1	1A	23-Jul	6.4	0.51 ^b	23.1±0.3	51±1
GPC-1	1B	25-Aug	10	0.53 ^b	22.1±0.5	59±2
GPC-3	1C	31-Jul	6.0	0.52 ^b	23.2±0.3	63±1
GPC-4	1D	01-Aug	6.6	0.52	23.3±0.4	62±1
<i>Counter cleaning with scrub and rinse, full strength product; towels retained</i>						
GPC-1	1E	28-Aug	9.9	0.53	22.0±0.2	58±1
GPC-3	1F	04-Sep	6.0	0.53	21.9±0.4	63±1
GPC-3	1G	10-Sep	6.0	0.51	21.9±0.4	60±6
GPC-3	1H	30-Sep	5.9	0.52 ^b	22.0±0.2	55±1
GPC-4	1I	09-Sep	6.6	0.54	22.0±0.2	67±5
GPC-4 ^c	1J	22-Dec	6.2	0.54	NA	NA
GPC-4	1K	23-Dec	5.7	0.55	20.8±0.1	41±1
<i>Counter cleaning, spray and wipe only, full strength product; towels retained</i>						
GLC-1	1L	02-Sep	6.5	0.52	22.1±0.2	66±2
GPC-2	1M	25-Sep	6.3	0.52	21.9±0.0 ^d	52±0 ^d
<i>Floor mopping, product diluted in 1 gal H₂O; towels retained</i>						
GPC-1	1N	18-Sep	50	0.51	21.9±0.4	35±3
GPC-3	1O	17-Sep	103	0.50	22.1±0.3	44±7
GPC-4	1P	16-Sep	53	0.55	22.0±0.2	51±2
GPC-4	1Q	29-Sep	153	0.52	21.9±0.3	54±3
<i>Air freshener: plugged in and operated on highest of three settings</i>						
AFR-1	1R	11-Sep	1.5 g/d	0.54	22.6±0.7	45±5

^a Air-exchange rates calculated from SF₆ concentration decay.^b Air-exchange measurement made on different day; air supply unaltered.^c Experiment aborted due to problems with T/RH data; VOC data available for first 4 h.^d Temperature and relative humidity data available for first 7 hours only.**Table 3.27.** Concentration (g L⁻¹) of d-limonene and ethylene-based glycol ethers in five cleaning products determined by direct analysis of product diluted in methanol.^a

Product	n	d-Limonene	2-BE	2-HE
GLC-1	4	-	6.0 ± 1.3	3.7 ± 1.5
GPC-1	3	14.7 ± 1.5	-	-
GPC-2	5	-	26 ± 4	-
GPC-3	7	-	62 ± 10	-
GPC-4	4	44 ± 5	31 ± 6	-

^a Results presented as mean ± one standard deviation, where n is number of diluted samples prepared; multiple injections from same dilution were averaged. 2-BE = 2-butoxyethanol; 2-HE = 2-hexyloxyethanol.

Table 3.28. Composition of GPC-1 determined by direct analysis of product diluted in methanol.^a

Analyte ^b	CAS #	RT (min) ^c	Concentration (mg mL ⁻¹)
<i>Terpene hydrocarbons</i>			
α -Pinene	80-56-8	21.8	1.1 \pm 0.6
Camphene	79-92-5	22.8	1.2 \pm 0.1
β -Pinene	127-91-3	24.0	0.13 \pm 0.01
α -Phellandrene ^d	99-83-2	25.1	0.42 \pm 0.13
α -Terpinene	99-86-5	25.6	2.5 \pm 0.7
d-Limonene	5989-27-5	25.9	14.7 \pm 1.5
γ -Terpinene	99-85-4	27.0	1.8 \pm 0.2
Terpinolene	586-62-9	27.9	23 \pm 3
<i>Terpene alcohols</i>			
1-Terpineol ^d	586-82-3	31.9	8.3 \pm 1.2
β -Terpineol ^d	138-87-4	32.7	4.6 \pm 0.7
4-Terpineol ^d	562-74-3	33.1	3.0 \pm 0.4
α -Terpineol	98-55-5	34.0	67 \pm 11
γ -Terpineol	586-81-2	34.2	11 \pm 0.5
<i>Other VOCs^e</i>			
p-Cymene	99-87-6	26.6	1.9 \pm 0.7
Eucalyptol	470-82-6	26.7	4.1 \pm 0.1

^a Results presented as mean \pm one standard deviation for n=3 dilution mixtures.

^b Compounds listed in retention-time order, except for “other VOCs”. Four additional compounds, tentatively identified as terpene hydrocarbons (3) and a terpeneol isomer, were present at <0.1%. Identified analytes accounted for approximately 15% of the product mass.

^c GC/MS retention time; RT of internal standard (bromofluorobenzene) was 23.9 min.

^d Quantified by total ion current based on d-limonene response. Identity of α -phellandrene confirmed with pure standard; terpeneols tentatively identified by matching mass spectra to NIST database. Uncertainty in TIC quantitation estimated as \pm 30% or less. 4-Terpeneol may be biased high because of a potentially co-eluting compound.

^e Selected VOCs; other compounds identified in product include 2-propanol, borneol, camphor, and isoborneol.

Table 3.29. Composition, chamber air concentrations, and emission rates for terpenoids and other VOCs in scented-oil air freshener, AFR-1.

Analyte	CAS #	RT (min)	Composition (mg mL ⁻¹) ^{a, g}	Concentration (μg m ⁻³) ^b	Emission rate (mg d ⁻¹) ^c
<i>Unsaturated (ozone-reactive) VOCs^d</i>					
d-Limonene	5989-27-5	25.9	17	35	39
Dihydromyrcenol ^e	18479-58-8	29.7	71	160	180
Linalool	78-70-6	30.6	65	132	148
Linalyl acetate ^e	115-95-7	34.5	25	56	63
β-Citronellol	7540-51-4	35.1	23	30	34
α-Citral	141-27-5	37.0	6.2	6.8	7.7
<i>Other VOCs^f</i>					
3,7-Dimethyl-3-octanol ^e	78-69-3	30.2	40	87	98
Benzyl acetate	140-11-4	33.4	136	280	320
Bornyl acetate	76-49-3	36.3	47	410	460

^a Composition determined by analysis of product diluted in methanol (mean of 2 determinations).

^b Time-averaged concentration over first 3 days of use in chamber calculated by linear interpolation between sampling points. See also Figure 3.7.

^c Mean emission rate over first 3 days of use in large-chamber experiments.

^d In addition to the compounds shown, β-pinene was quantified at ~1.5 mg mL⁻¹ in composition experiments. Concentrations and calculated emissions during product-use experiments were consistent with this value; precise determination was precluded owing to high background levels.

^e Quantified by total ion current based on d-limonene response; uncertainty estimated as ±30% or less. Compound identities confirmed with pure standards.

^f Selected prominent VOCs. Other constituents identified and quantified with pure standards include phenylethyl alcohol (RT = 33.3 min, ~50 mg mL⁻¹) and trans-4-tert-butylcyclohexyl acetate (RT = 38.5 min, ~10 mg mL⁻¹). Constituents tentatively identified by matching mass spectra to NIST database and quantified by TIC response include isononyl acetate (RT = 32.0 min, ~50 mg mL⁻¹) and α,α-dimethylbenzene ethanal acetate (RT = 37.5 min, ~100 mg mL⁻¹).

^g Positively and tentatively identified analytes together accounted for approximately 65% of the product mass.

Table 3.30. Emission factors and initial chamber air concentrations for d-limonene and ethylene-based glycol ethers associated with simulated cleaning activities. ^a

Product	Expt	Emission factor (mg per g product)			Chamber air concentration 0-1 h ($\mu\text{g m}^{-3}$)		
		Lim	2-BE	2-HE	Lim	2-BE	2-HE
<i>Counter: full strength with scrub and rinse; towels removed</i>							
GLC-1	1A	-	2.6	1.9	-	270	170
GPC-1	1B	6.8	-	-	960	-	-
GPC-3	1C	-	25	-	-	2300	-
GPC-4	1D	22	7.4	-	2200	720	-
<i>Counter: full-strength with scrub and rinse; towels retained</i>							
GPC-1	1E	10.2	-	-	1100	-	-
GPC-3 ^b	1F-1H	-	34±1	-	-	1600±80	-
GPC-4 ^c	1I-1K	30, 32	15, 16	-	2500±70	680±50	-
<i>Counter: full-strength, spray and wipe only; towels retained</i>							
GLC-1	1L	-	8.0	4.8	-	330	190
GPC-2	1M	-	30	-	-	1410	-
<i>Floor mopping with dilute solution</i>							
GPC-1	1N	1.6	-	-	1130	-	-
GPC-3	1O	-	1.3	-	-	1300	-
GPC-4 ^d	1P	3.7	0.7	-	2900	380	-
GPC-4 ^d	1Q	2.7	0.7	-	6200	1150	-

^a Net 24-h emission factors and 1-h-average gas-phase concentrations beginning when cleaning commenced; Lim = d-limonene, 2-BE = 2-butoxyethanol, 2-HE = 2-hexyloxyethanol.

^b Results (mean \pm standard deviation) are from three experiments, 1F-1H.

^c Results are from two experiments (1I, 1K) in the case of emissions, and from three experiments (1I-1K) in the case of the first-hour average concentrations.

^d Experiments conducted with different product dilutions; see Table 3.26.

Table 3.31. Emission factors and initial chamber air concentrations of terpenes and terpene alcohols associated with use of GPC-1.^a

Analyte	Emission factor (mg per g product)			Chamber air concentration 0-1 h ($\mu\text{g m}^{-3}$)		
	Exp 1B Counter	Exp 1E Counter	Exp 1N Floor	Exp 1B Counter	Exp 1E Counter	Exp 1N Floor
<i>Terpene hydrocarbons</i>						
α -Pinene	0.41	0.56	0.09	58	74	66
Camphene	0.61	0.84	0.14	87	109	105
β -Pinene	0.09	0.06	0.01	12	14	13
α -Phellandrene ^b	0.14	0.24	0.04	23	29	29
α -Terpinene	0.49	0.89	0.16	90	113	124
d-Limonene	6.8	10.2	1.6	960	1100	1130
γ -Terpinene	0.66	1.15	0.17	95	112	120
Terpinolene	5.5	10.3	1.8	890	1040	1270
<i>Terpene alcohols</i>						
1-Terpineol ^b	0.52	1.8	0.37	57	75	160
β -Terpineol ^b	0.30	0.85	0.18	39	41	75
4-Terpineol ^b	0.27	0.89	0.15	44	48	74
α -Terpineol	2.8	7.4	2.3	260	340	700
γ -Terpineol	0.26	0.79	0.25	31	41	93
<i>Other VOCs</i>						
p-Cymene	1.04	1.63	0.25	142	172	174
Eucalyptol	1.80	3.0	0.45	250	300	330

^a Net 24-h emission factors and 1-h-average gas-phase concentrations beginning when cleaning commenced. Experiments 1B and 1E simulated cleaning of laminate tabletop using full-strength product; paper towels were removed after cleaning in experiment 1B and retained throughout in experiment 1E. In experiment 1N, product was diluted in water and used to mop floor.

^b Quantified by total ion current based on d-limonene response. Identity of α -phellandrene confirmed with pure standard; terpineols tentatively identified by matching mass spectra to NIST database. Uncertainty in TIC quantitation estimated as $\pm 30\%$ or less. 4-Terpineol may be biased high because of a potentially co-eluting compound.

Table 3.32. Summary of key California consumer product regulations concerning the reactive volatile organic compound content of cleaning product classes included in the present study. ^{a, b}

Cleaning product	Packaging	VOC limit ^c	Date
Disinfectant		N/A	
General purpose degreaser ^d	Aerosol	50%	1/02
General purpose degreaser ^d	Nonaerosol	4%	12/04
General purpose cleaner	Aerosol	10%	1/94
General purpose cleaner	Nonaerosol	4%	12/04
Glass cleaner	Aerosol	12%	1/93
Glass cleaner	Nonaerosol	4%	12/04
Wood cleaner	Aerosol	17%	12/06
Wood cleaner	Nonaerosol	4%	12/06
Furniture maintenance products	Aerosol	17%	12/04
Furniture maintenance products	Nonaerosol	7%	1/94
Spot remover	Aerosol	25%	1/01
Spot remover	Nonaerosol	8%	1/01
Multi-purpose solvent		N/A	

^a Source: CARB, 2005a.

^b Reactive volatile organic compound content is defined in terms of its potential to contribute to urban photochemical smog. Species such as methane and chlorinated organic compounds are exempted from this class because of their low rates of photochemical reactivity.

^c “For consumer products for which the label, packaging, or accompanying literature specifically states that the product should be diluted with water or non-VOC solvent prior to use, [these limits] shall apply to the product only after the minimum recommended dilution has taken place.” Such minimum recommended dilution “shall not include recommendations for incidental use of a concentrated product to deal with limited special applications such as hard-to-remove soil or stains.” (CARB, 2005a, §94509(b)).

^d In addition to limiting their VOC content, as of December 2005, general purpose degreasers sold in California are specifically prohibited from containing more than trace impurity levels of methylene chloride, perchloroethylene, and trichloroethylene.

Table 3.33. Summary of findings from composition characterization and primary emissions experiments.

-
- **Product selection for composition characterization.** A multistage shelf-inventory and screening process was used to select 21 cleaning products and air fresheners that would be commonly available to California consumers and that were suspected to contain either ethylene-based glycol ethers or terpenes or other ozone-reactive constituents.
 - **Composition characterization.** The chemical composition of the 21 products was characterized in laboratory experiments. Six products contained glycol ethers, primarily 2-butoxyethanol, at levels ranging from 0.8-9.6%. The only other toxic air contaminant detected was xylene in one furniture maintenance product. Four cleaning products contained substantial quantities of d-limonene, an ozone-reactive terpene, in the range 3.9-25%. Three cleaning products contained pine oil constituents, including a suite of terpene hydrocarbons and terpene alcohols. Five cleaning products had less than 0.2% by mass of any individual target compound. Three of the four air fresheners contained substantial mass fractions (9-14%) of terpenes and related compounds. (Tables 3.11-3.15)
 - **Product selection for simulated-use experiments:** Six of the products were selected for simulated use experiments in a room-sized chamber. Four of the products (one glass cleaner and three general-purpose cleaners) were selected because of their glycol ether content. One of these also contained d-limonene. Two additional products were selected because of their terpene content, a pine-oil based general purpose cleaner, and a plug-in scented air freshener. (Table 3.25)
 - **Simulated-use experiments.** Eighteen simulated use experiments were conducted in a 50-m³ chamber with a controlled air-exchange rate of 0.5 per hour. These experiments entailed either full-strength use in counter-cleaning applications (13 experiments), dilute use in floor-mopping applications (4 experiments), or ordinary use of a plug-in air freshener (1 experiment). In these experiments, concentrations of component chemicals were measured and emission factors were computed from a material balance model. (Table 3.26)
 - **2-Butoxyethanol results.** For the products that contained 2-butoxyethanol (2-BE), peak one-hour-average concentrations in chamber air after simulated use varied in the range 270-2300 $\mu\text{g m}^{-3}$. The corresponding emission factors were in the range 0.7-34 mg of 2-BE emitted per g of cleaning product used. (Table 3.30)
 - **d-Limonene results.** For the products that contained d-limonene, peak one-hour-average concentrations in chamber air after simulated use varied in the range 960-6200 $\mu\text{g m}^{-3}$. Emission factors were in the range of 1.6 to 32 mg of d-limonene emitted per g of cleaning product used. (Table 3.30)
 - **Effect of towel retention on fractional emissions.** Fractional emissions of 2-butoxyethanol and d-limonene from full-strength use were 50-100% with towels retained in the room, but only 25-50% when towels were removed after cleaning. (Figure 3.8)
 - **Pine-oil cleaner results.** For the pine-oil based cleaning product, we quantified concentrations and emissions of 15 constituents, including eight terpene hydrocarbons and five terpene alcohols. The most prominent species were d-limonene and terpinolene, which reached peak one-hour-average concentrations of 890-1270 $\mu\text{g m}^{-3}$. Peak concentrations for the other compounds were in the range 10-700 $\mu\text{g m}^{-3}$. (Table 3.31)
-

Table 3.33. (continued)

-
- **Emissions from dilute use.** Dilute use of cleaning products for floor-cleaning yielded much lower fractional emissions (2-11% for 2-BE and d-limonene, 7-12% for terpene hydrocarbons, and 2-5% for terpene alcohols) than did full strength use for counter cleaning. (Figures 3.8-3.9)
 - **Scented-oil air freshener results.** For the scented-oil air freshener, the experiment involved continuous use for a three-day period. We quantified concentrations and emissions of 9 compounds, including six unsaturated compounds that could potentially react with ozone. The most prominent of the unsaturated compounds were dihydromyrcenol and linalool, for which the 3-day average room air concentrations were 160 and 132 $\mu\text{g m}^{-3}$, respectively. (Table 3.29)
-

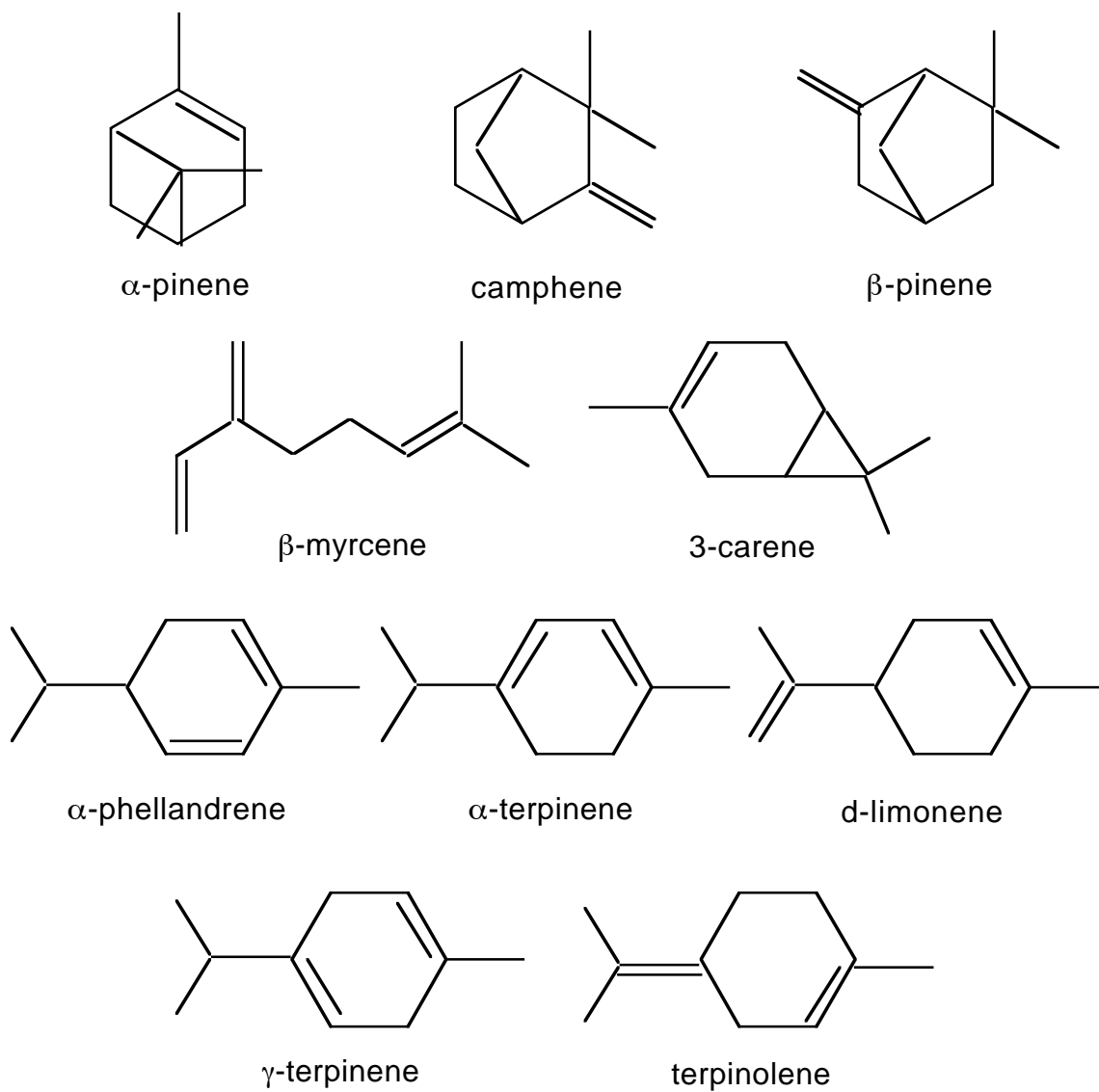


Figure 3.1. Chemical structure of terpene hydrocarbons included among target analytes.

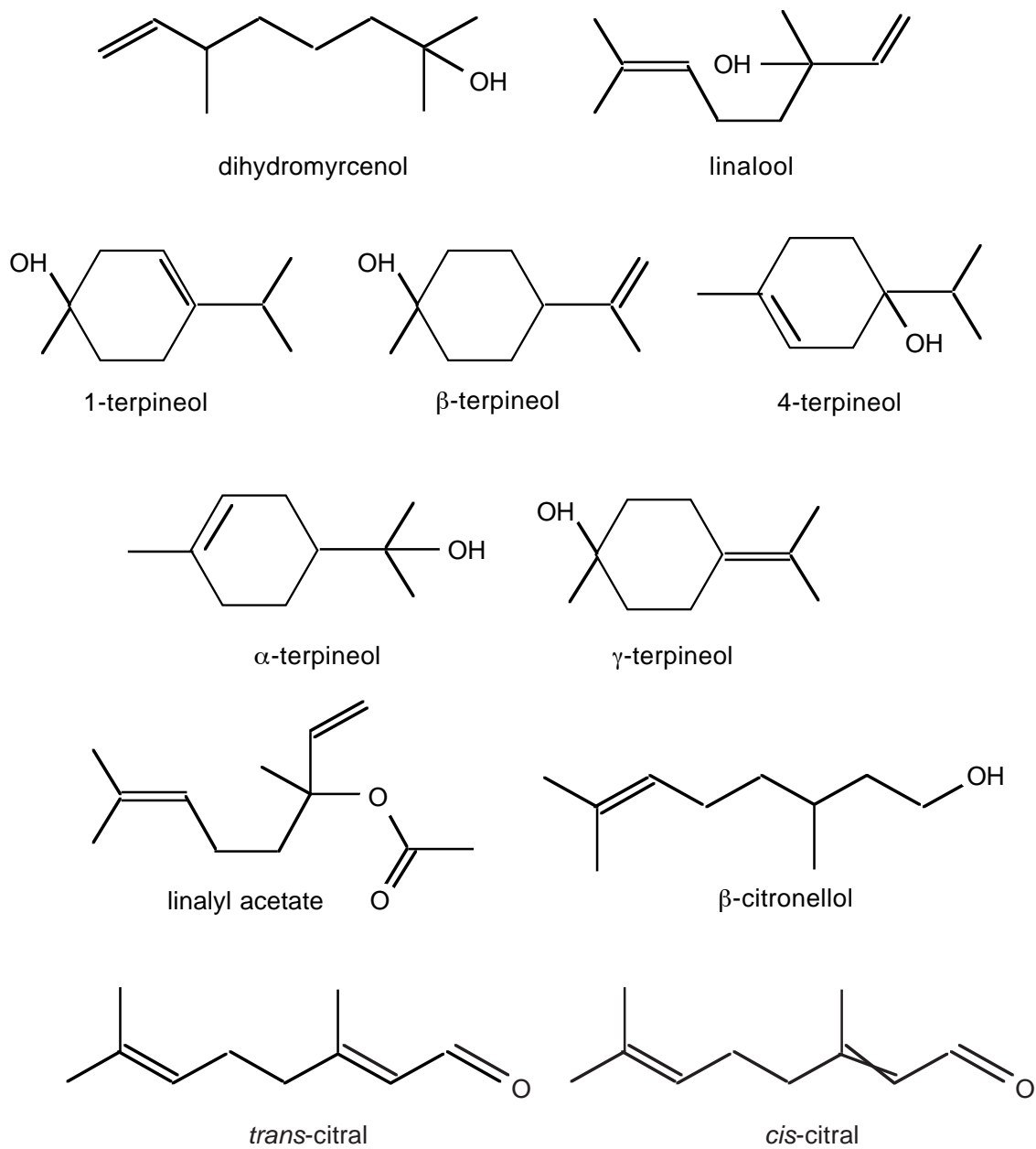
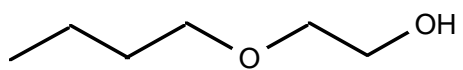
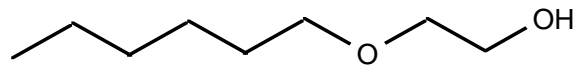


Figure 3.2. Chemical structure of unsaturated, oxygenated compounds include among target analytes.



2-butoxyethanol



2-hexyloxyethanol

Figure 3.3. Chemical structure of ethylene-based glycol ethers included among target analytes.

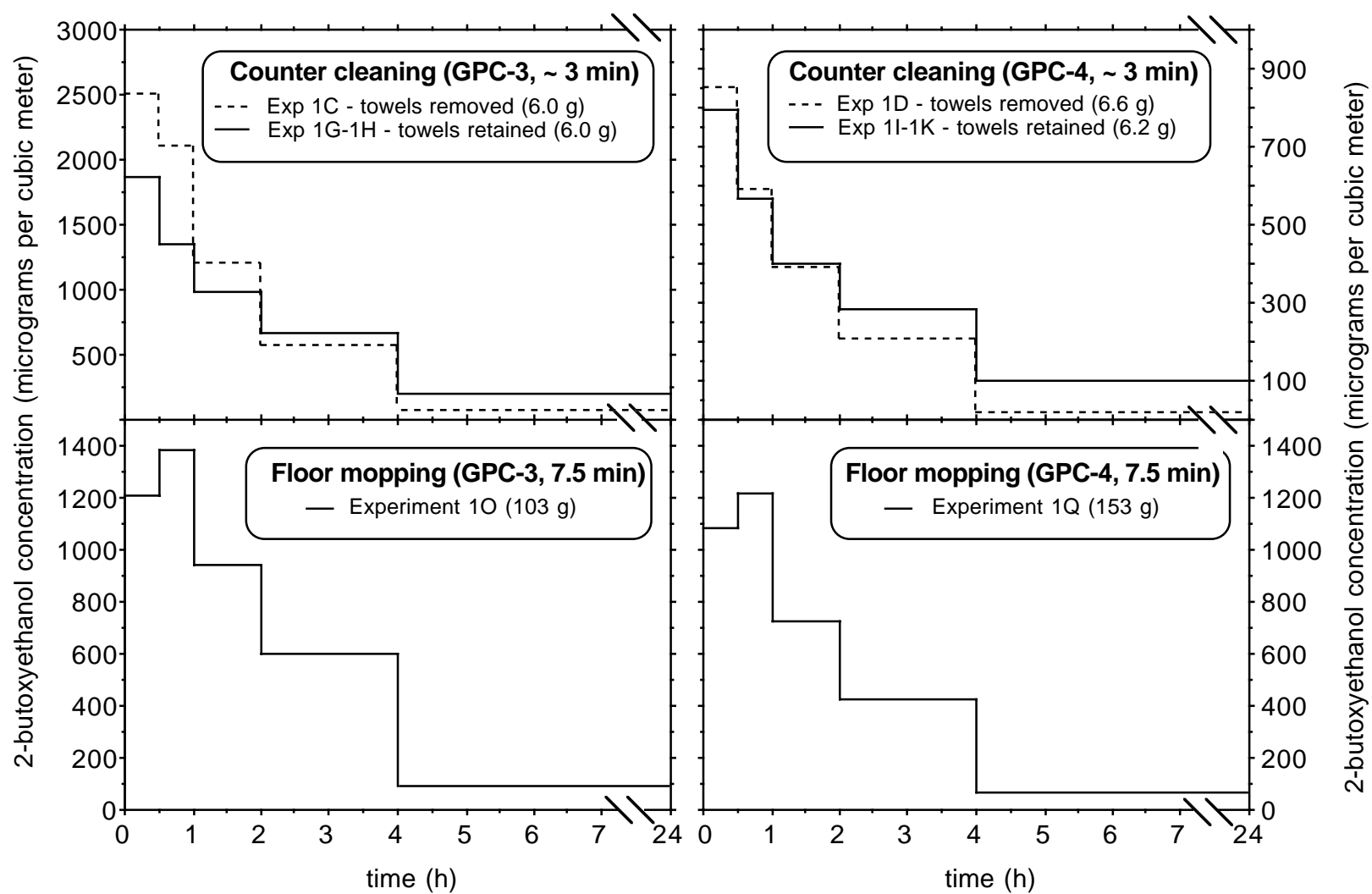


Figure 3.4. Measured concentrations of 2-butoxyethanol following simulated use of GPC-3 and GPC-4 in selected large-chamber experiments.

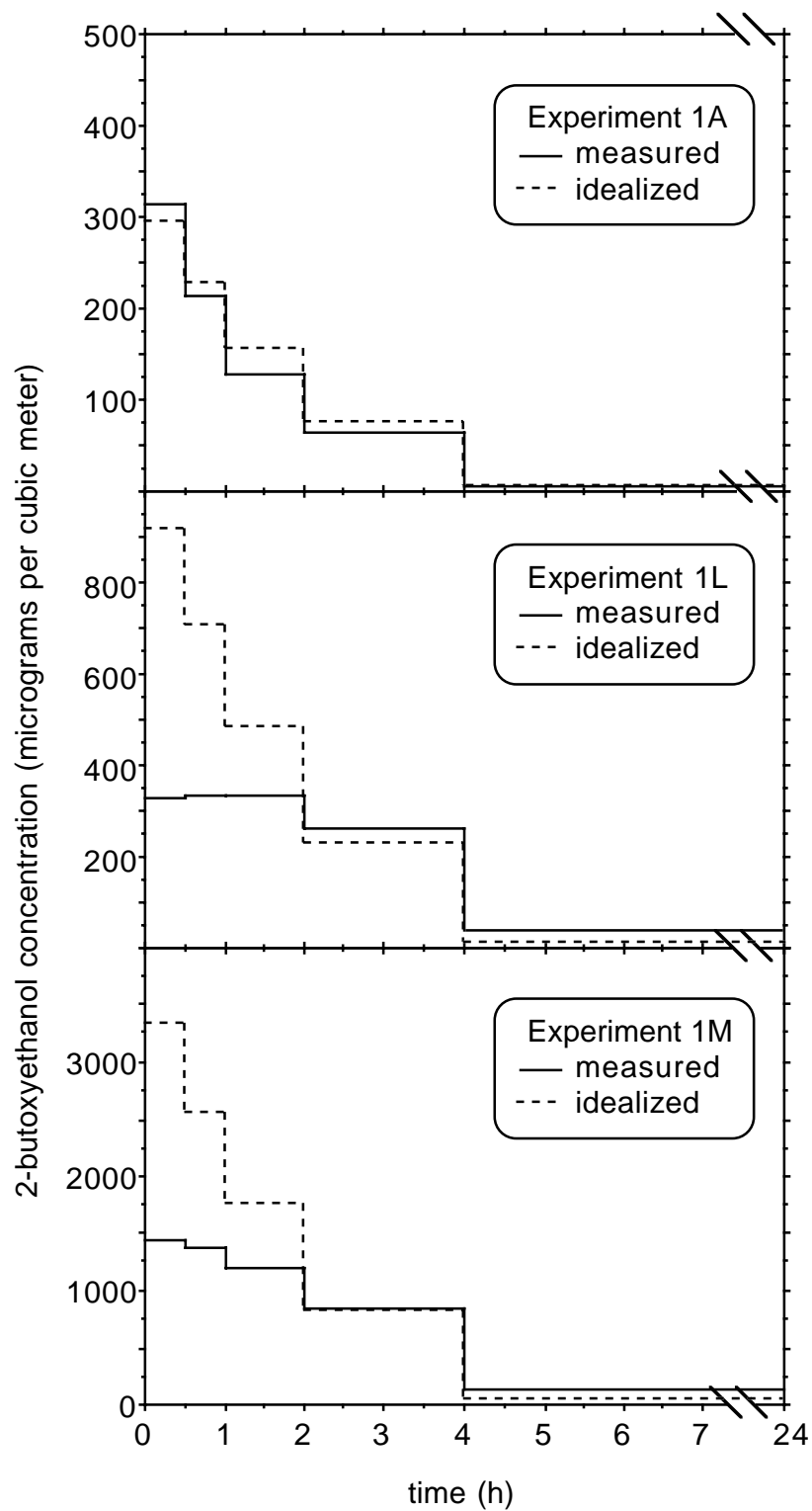


Figure 3.5. Measured concentrations of 2-butoxyethanol following simulated use of GLC-1 (Experiments 1A & 1L) and GPC-2 (Experiment 1M) in large chamber experiments and idealized theoretical time profiles.

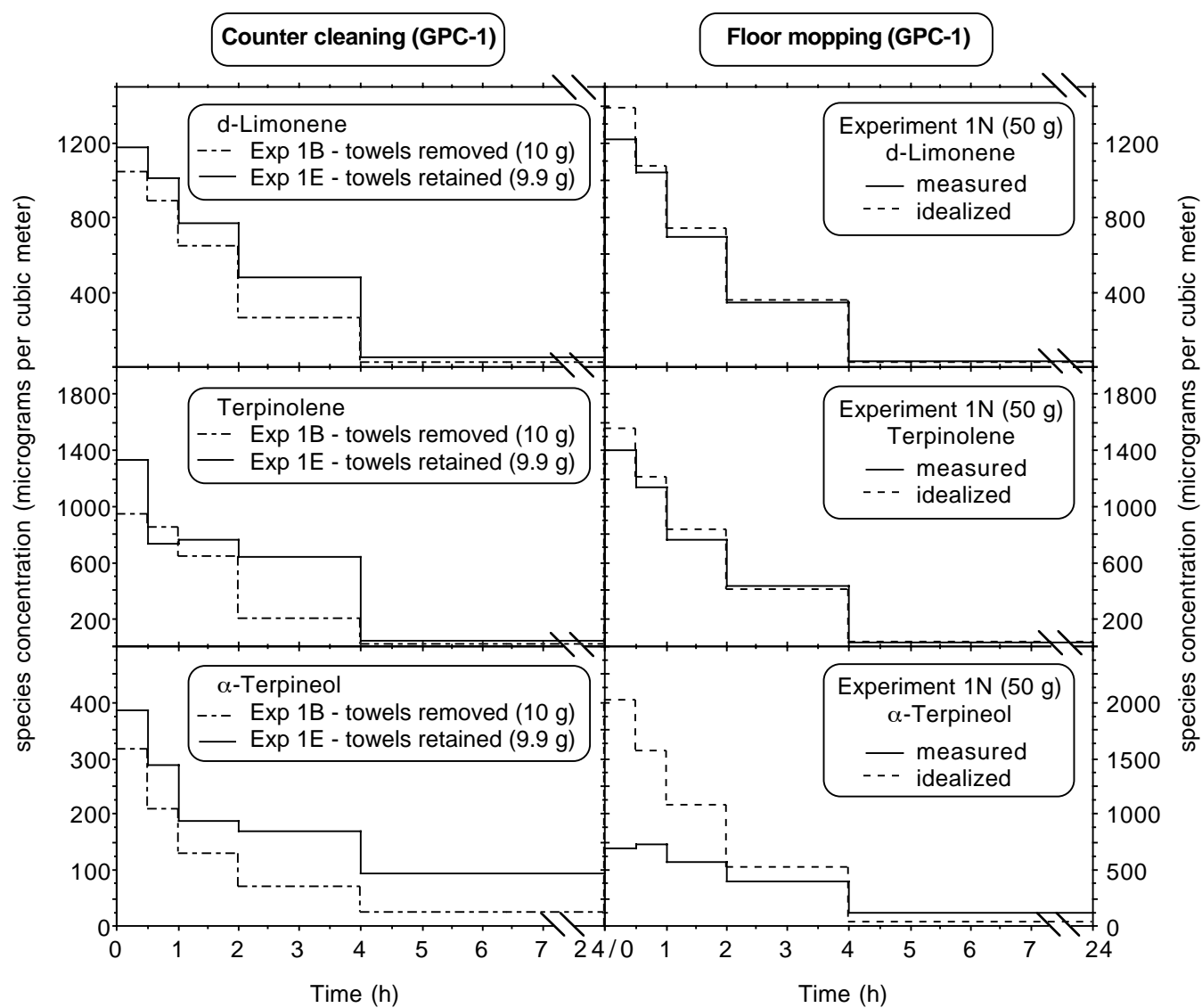


Figure 3.6. Measured concentrations of major terpene and terpene alcohol constituents following application of GPC-1 in large-chamber experiments.

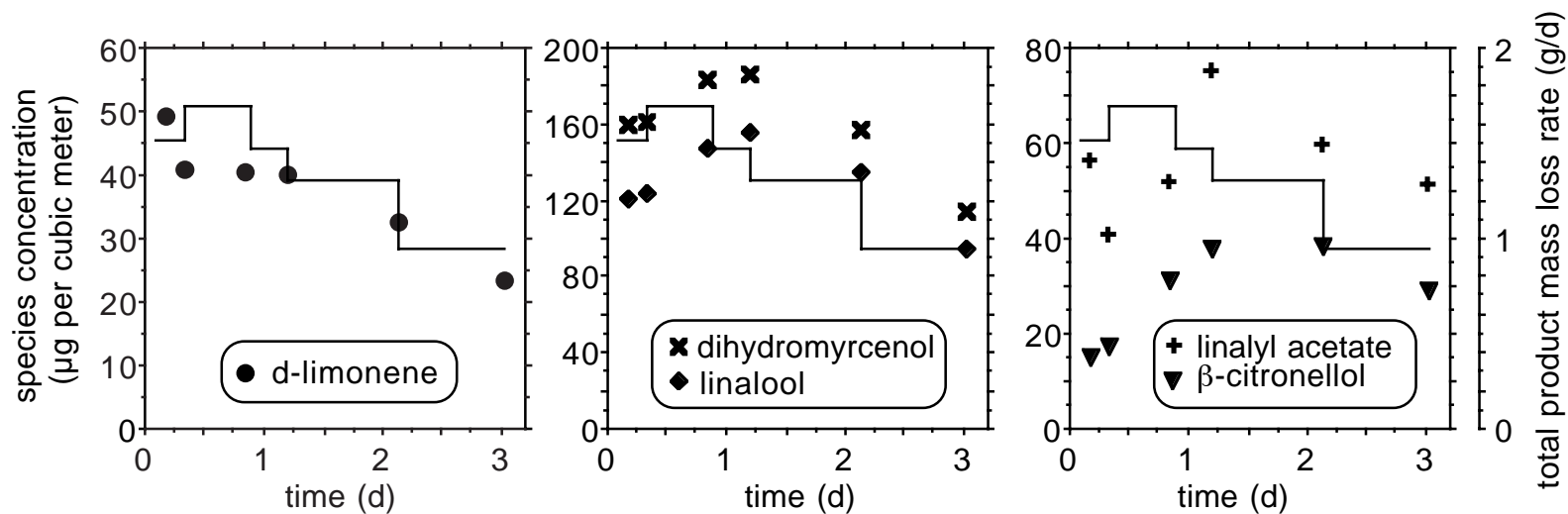


Figure 3.7. Results of experiment 1R, using scented-oil air freshener, indicating time-dependent concentrations of selected unsaturated organic compounds (symbols) and total rate of air freshener product volatilization (lines).

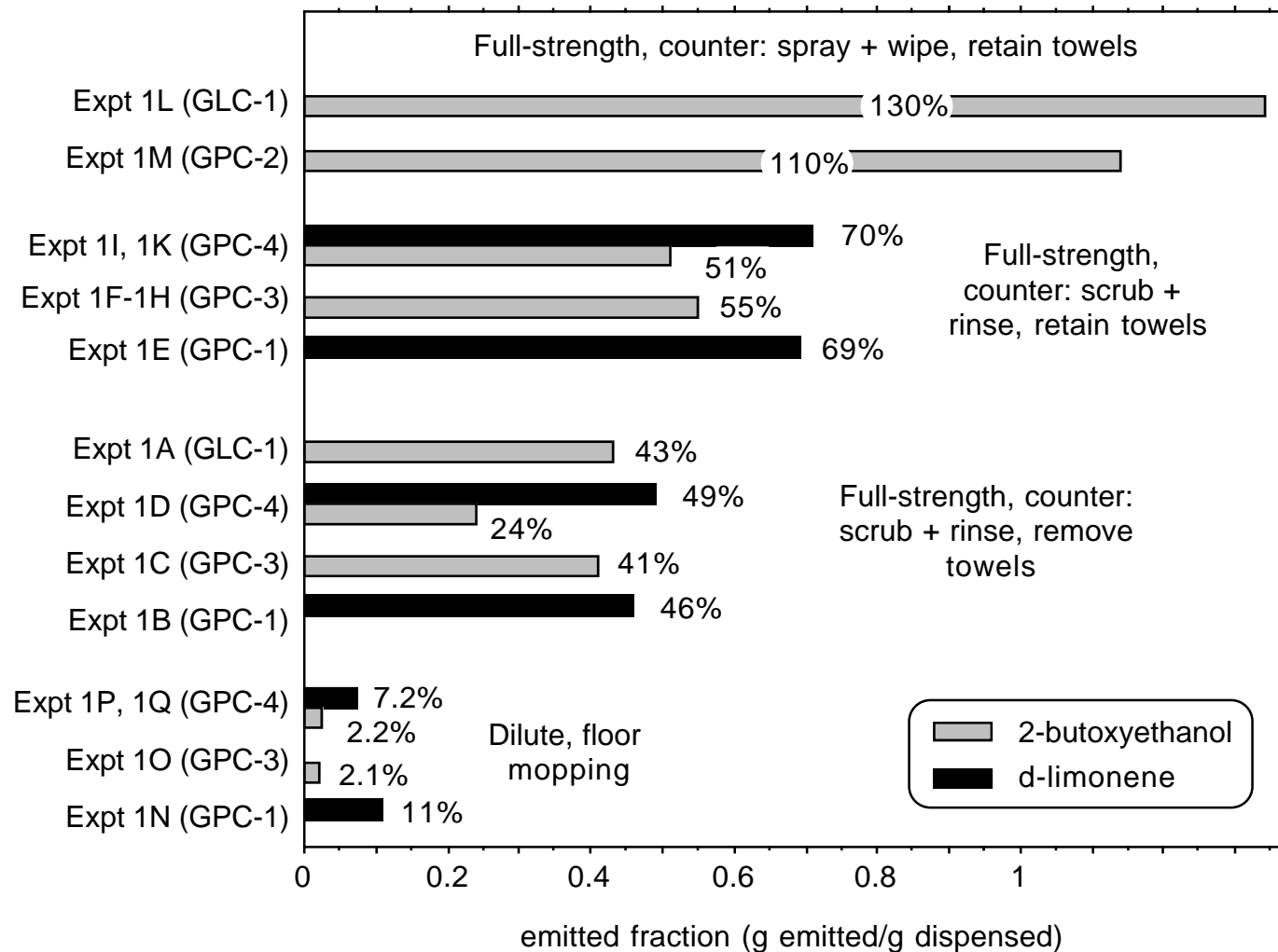


Figure 3.8. Emitted fraction of 2-butoxyethanol and d-limonene for cleaning-product experiments conducted in a 50-m³ chamber.

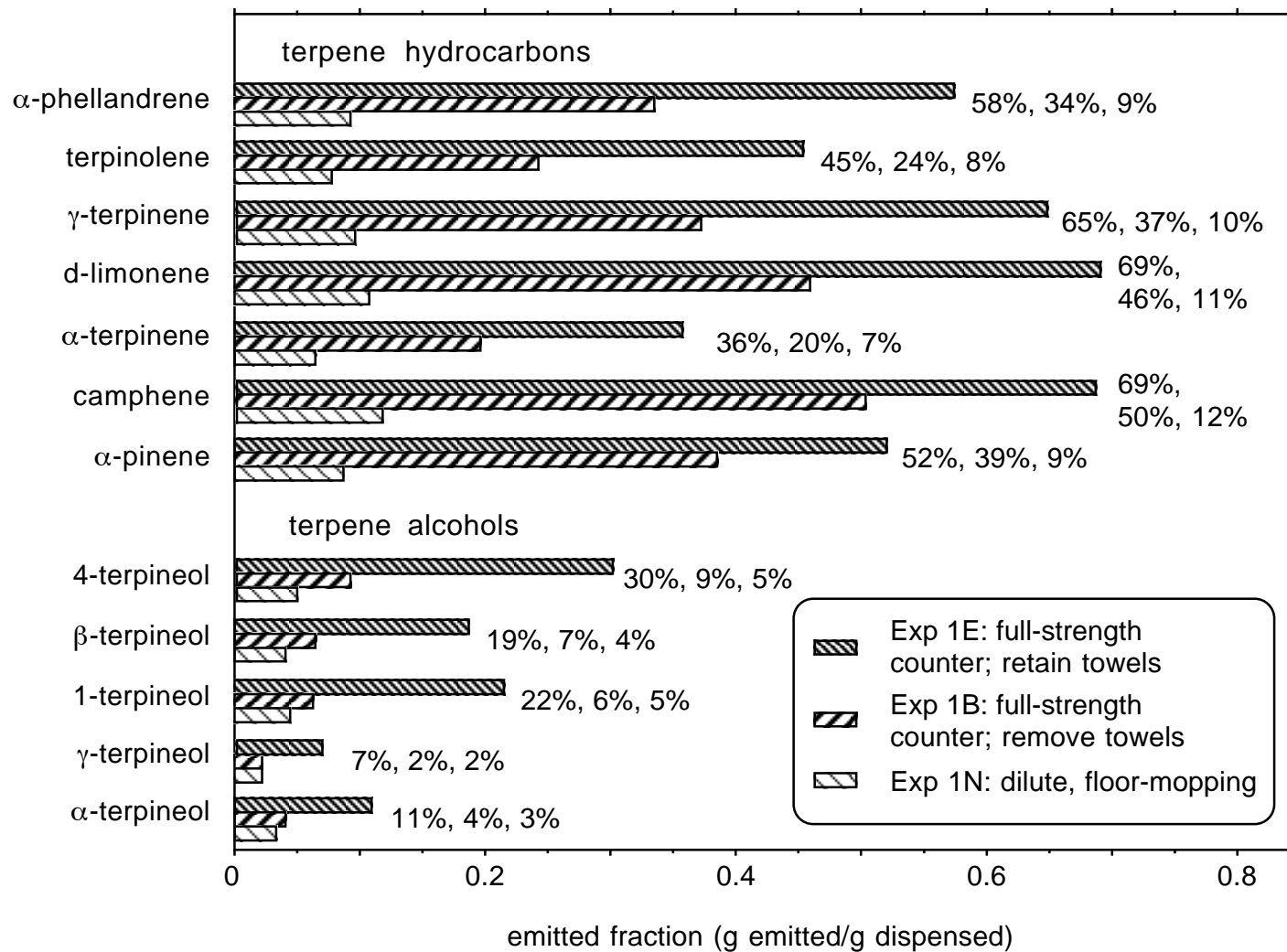


Figure 3.9. Emitted fraction of terpenes and terpene alcohols associated with use of cleaning product GPC-1.

4. REACTIVE CHEMISTRY INVOLVING CONSTITUENTS OF CLEANING PRODUCTS AND AIR FRESHENERS

4.1. Introduction

As reviewed in §2, the use of cleaning products and air fresheners indoors can cause inhalation exposure of cleaning personnel and building occupants to toxic air contaminants (TACs). In addition to direct inhalation of toxic constituents, many products contain terpene hydrocarbons and other terpenoids that can react rapidly with ozone yielding secondary pollutants, including secondary organic particulate matter. Ozone is commonly present indoors owing to intrusion from outdoor air. Indoor sources of ozone also exist, including certain “air purifiers” that can generate indoor ozone levels on the order of hundreds of ppb (Boeninger, 1995). The products of ozone reactions with terpenes and terpenoids include volatile carbonyls, some of which are TACs (e.g., formaldehyde and acetaldehyde). Ozone-terpene reactions also produce the hydroxyl radical (OH), which potentially can lead to the formation of additional TACs (Atkinson, 1997).

Little is known about the indoor concentrations of TACs that are formed as secondary pollutants from cleaning products and air fresheners. Indoor concentrations of such secondary pollutants depend on the complex interplay of many factors and processes, including product composition, usage, emission dynamics, transport and mixing, building ventilation, sorptive interactions with building surfaces, and reactive chemistry. In this section of the report, we describe two sets of experiments designed to provide new data on the interactions of ozone with terpene-containing cleaning products and air fresheners. The overarching goal is to provide information relevant to understanding human inhalation exposures that result from indoor use of such products. The first set of experiments, described in §4.2-4.3, was conducted under highly controlled conditions with steady flows through a bench-scale environmental chamber. The second set of experiments, described in §4.4-4.5, was carried out through simulated use of the products, with or without the presence of ozone, in a room-sized research chamber.

4.2. Bench-Scale Chamber Experiments: Methods

4.2.1. Reaction chamber and ancillary setup

The reaction of ozone with cleaning product and air freshener components was studied in a 198-L stainless-steel flow reaction chamber, internally lined with FEP-Teflon film. The chamber was operated under positive pressure. It was configured with two inlet ports on opposite corners and an outlet port. A constant flow of air and the product gas-phase components was introduced into one port, and an air stream containing ozone was admitted at the other inlet. Chamber temperature and relative humidity (RH) were measured and continuously recorded. The experimental apparatus was housed in a 20-m³ environmental room maintained at 23.0 ± 0.5 °C. The main airflow to the chamber, of compressed “zero quality” air, was split between a dry and a humidified stream and adjusted using mass-flow controllers to obtain an RH between 40 and 60%. Well-mixed conditions within the chamber were demonstrated with SF₆, which was introduced at either inlet and continuously monitored at the outlet using an infrared analyzer during chamber-characterization experiments. The all-Teflon reactor limited the surface interactions of the studied chemicals, including ozone decomposition on chamber materials.

Ozone (O₃) was generated by means of UV irradiation of an airstream flowing at 100 mL/min. Immediately before and after each run, the ozone inlet concentration was measured by means of a calibrated ozone monitor to determine the amount of O₃ introduced in the chamber and to verify its stability. Otherwise, the ozone monitor continuously sampled from the chamber

outlet and the data were logged at 1-min intervals. In preliminary runs, we verified that inlet concentrations accurately represented ozone chamber concentrations in the absence of VOCs. Flows of background air, product components and ozone were measured before and after the experiments with a precision of better than 2%.

4.2.2. Characterization and delivery of household products emissions

Three common retail products sold in California and containing ozone-reactive chemicals were employed: a general-purpose pine oil-based cleaner (GPC-1), an orange oil-based degreaser containing d-limonene as the sole active ingredient (GPD-1), and a plug-in scented-oil air freshener (AFR-1). Gas-phase components of the first two products were delivered to the reaction chamber from an 80-L Tedlar bag prepared by adding a measured amount of the product and air, heating in an incubator at 50 °C for 2 h, and then cooling to room temperature. A peristaltic pump delivered a constant flow (in the range 20-100 mL/min) into the main airflow. For the air freshener, an 80-L stainless steel drum replaced the Tedlar bag. Inside the drum, the product was continuously electrically powered, as in ordinary use, and a stream of air flowing at 100 mL/min introduced the volatile components into the main air stream. Experiments were designed to replicate VOC concentrations determined during realistic use of the products in a 50-m³ room, as described in §3.

Composition of the gas-phase emissions from the selected products was determined in earlier phases, as reported in §3.3.3 and §3.4.3. The three main volatile ingredients of GPC-1 were d-limonene, terpinolene and α -terpineol. Other monoterpenes were detected in smaller quantities (α - and γ -terpinene, α - and β -pinene, camphene, γ -terpineol and α -phellandrene), together with additional VOCs (p-cymene, eucalyptol). Organic emissions from GPD-1 were exclusively d-limonene. More than 30 volatile components were detected from AFR-1, including d-limonene and a variety of alcohols (linalool, dihydromyrcenol, β -citronellol) and esters (linalyl acetate, bornyl acetate).

4.2.3. Sampling and analytical methods

VOCs were sampled onto Tenax®-TA sorbent tubes connected in parallel immediately after the outlet port. Two adjacent sampling ports were used to collect samples on DNPH-coated silica cartridges preceded by an ozone scrubber to determine volatile carbonyl compounds and on NaOH-coated silica cartridges to determine volatile carboxylic acids. Ozone scrubbing was determined to be unnecessary for the VOCs by collecting simultaneous samples of different volumes.

VOCs collected in Tenax sorbent tubes were analyzed by thermal desorption-gas chromatography-mass spectrometry (TD-GC/MS) using an HP6890 GC equipped with a Chrompack TCT 4020 desorber with cryogenic trap and interfaced to an HP5973 mass selective detector (MSD) that operated in electron impact mode. Details of the GC-MSD method are given in §3.3.2 and were previously described (Singer et al., 2002 and 2004). DNPH-coated cartridges were extracted with 2 mL acetonitrile. DNPH-carbonyl derivatives present in the extracts were analyzed at 360 nm by HPLC provided with a UV detector. NaOH-coated silica cartridges were extracted with deionized water, and the extracts were analyzed by ion chromatography.

4.2.4. Experimental matrix

Table 4.1 provides an overall summary of the fifteen experiments conducted in this phase of the research. We investigated the effect of two parameters on each of the three products:

reaction time using air exchange rates of 1 per hour (h^{-1}) and 3 h^{-1} , and the ozone level using 110-140 ppb (high) and 60-70 ppb (moderate) inlet concentrations. One of these experiments (2B) was run in triplicate to explore experimental reproducibility. In addition to this set of nine experiments (2A-2C and 2F-2K), the effects of low (~ 30 ppb) and very high (~ 250 ppb) inlet O_3 levels were investigated with the GPC-1 product (experiments 2D and 2E). Three additional experiments (2L-2N) were carried out by means of exposing to ozone a surface residue of each of the products. In the final experiment (2O), the GPC-1 product was exposed to both ozone and nitrogen dioxide.

4.2.5. *Experimental procedure*

VOC concentrations in the reaction chamber were established without ozone supply by feeding air from the source container into the reaction chamber. After steady-state conditions were established, the VOC concentrations were determined during the first 2-4 h of each experiment. Subsequently, ozone was introduced at a constant flow rate and VOC concentrations were again measured once steady state was achieved. Reactant consumption and product yields were calculated by difference.

4.2.6. *Determination of OH radical concentration*

We adopted a method used by Weschler and Shields (1997a) to indirectly determine the OH concentration. A stream of 1,3,5-trimethylbenzene (TMB) and perchloroethylene (PCE) was generated with diffusion tubes placed in a thermostat at 40°C and supplied at a constant rate to the reaction chamber. The TMB/PCE ratio was used to estimate the concentration of OH in the system, assuming that TMB reacted significantly with OH but negligibly with O_3 at our short residence times; PCE served as a nonreactive reference tracer. Both chemicals were sampled on Tenax sorbent tubes in the absence and presence of ozone, and analyzed by TD-GC/MS.

4.2.7. *Particle sampling*

An opportunity arose to sample particle size distributions in chamber air with a scanning mobility particle sizer (SMPS) system that utilized a differential mobility analyzer (Model 3071A, TSI Inc.) coupled with a condensation particle counter (Model 3760, TSI Inc.). The system was configured to measure particle sizes from 8 to 412 nm. Size distributions were obtained at 1-min intervals using software developed by D Collins (Texas A&M University) and P Chuang (UCSC). For selected experiments, an optical particle counter (OPC; Lasair 1003, Particle Measuring Systems, Inc.) was also employed to extend the particle size range up to $2 \mu\text{m}$. Aerosol particle sampling was performed continuously, starting before the introduction of ozone.

4.2.8. *Surface residue experiments*

The reactions of ozone with semivolatile or nonvolatile components of the products were investigated in Experiments 2L-2M. The cleaning products (GPC-1 and GPD-1) were evaluated through application of a 0.5-mL aliquot to one side of a 0.09 m^2 glass plate. After removing the excess liquid, the plate was placed in a 10-L stainless-steel cell and exposed for 1.5 h to a N_2 flow at an air-exchange rate of 3 h^{-1} to remove the more volatile components. At the end of the volatilization period, only α - and γ -terpineol were still evidently being emitted by the surface from the GPC-1 application, and no VOCs were detected for GPD-1. The plate was then placed in the 198-L reaction chamber, which had been previously conditioned at ~ 120 ppb O_3 , and

operated at an air-exchange rate of 1 h^{-1} . The plates were exposed to ozone under the same conditions for 24 hours. Chamber ozone and aerosol concentrations were monitored continuously starting before the introduction of the plate. VOC and carbonyl samples were collected periodically. For the air freshener, a sample was prepared by exposing for a two-day period the surface of a clean glass plate in the 80-L stainless steel drum where the product was continuously electrically powered. The plate was then removed from the drum and placed directly in the 198-L reaction chamber that had been previously conditioned at $\sim 120\text{ ppb O}_3$. The reaction chamber with the plate was operated at an air-exchange rate of 1 h^{-1} . The plate was exposed to ozone until chamber levels returned to those recorded previous to the introduction of the plate.

4.2.9. Experiments conducted in the presence of NO_2

In Expt 2O, we investigated the effect of added NO_2 on the studied ozone-VOC chemistry. This test was performed for GPC-1 components, with a high ozone concentration (130 ppb) and at 3 h^{-1} . Except for the addition of NO_2 , the experimental conditions were the same as in Expt 2B.

A stream of NO_2 was mixed with chamber air using a calibrator (Model 760, VICI Metronics). Inlet and chamber NO_2 and NO were continuously monitored with a chemiluminescence NO_x analyzer (Model 42, Thermo Environmental Instruments Inc.) and recorded at 10-s intervals. Sampling of VOCs, carbonyls, carboxylic acids and aerosol particles was performed in a similar manner as for the other experiments.

4.2.10. Data quality and uncertainty

Data quality procedures for the bench-scale chemistry experiments included evaluation of chamber blanks and collection of replicate samples when determining analyte concentrations under each condition. VOC samples were collected prior to the start of each experiment to quantify chamber air concentrations of product constituents. No measurable amounts of product constituent VOCs in the chamber were detected in any background sample. VOC samples were collected in 3-5 replicates for each experimental condition (i.e., before and after introduction of ozone and after establishment of steady-state conditions). The corresponding experimental uncertainties were determined from the standard deviation of the determinations under like conditions. Concentrations determined from extraction of DNPH-impregnated samplers (carbonyls) and NaOH-impregnated samplers (carboxylic acids) are reported as the average of two collocated determinations (in parallel); their corresponding experimental uncertainties are estimated as the standard deviation between the measured results.

4.3. Bench-Scale Chamber Experiments: Results and Discussion

4.3.1. Reactivity of primary constituents and ozone

In Figures 4.1-4.2 and Tables 4.2-4.4 we present data obtained from experiments with the three household products in the presence of various levels of ozone in supply air and at air-exchange rates of 3 h^{-1} and 1 h^{-1} . In the tables, the values shown in the concentration (C) columns are for ozone in the absence of reactive VOCs and for VOCs before addition of ozone. Oxidation product concentrations are those measured at steady state in the presence of ozone. For oxidation products that were present before ozone was added (acetone and acetic acid), the values reported in Tables 4.2-4.4 represent the increases owing to reaction, i.e., the difference between those measured with and without ozone. The adjacent data columns indicate the fractions of ozone and VOCs that reacted and the yields of oxidation products. A percent yield is the ratio of oxidation

product generated (ppb) to ozone consumed (ppb) during the reaction. Ozone consumption was calculated as the difference between inlet and outlet (residual) ozone levels. Figures 4.1 and 4.2 illustrate the VOC consumption and oxidation product yields for all conditions. In Figures 4.2A and 4.2C, total yields higher than 100% indicate that some products may have originated at more than one step in the oxidation sequence or that OH radicals generated in terpene-ozone reactions are involved in the production of additional oxidation products.

For the seven VOC components from the GPC-1 shown in Table 4.2, only one — α -terpinene — reacted substantially and unambiguously under all test conditions. Four compounds — d-limonene, terpinolene, and α - and γ -terpineols — reacted substantially in some, but not all test conditions. Eucalyptol and p-cymene were relatively inert, as expected based on their bimolecular rate constants with ozone. The results for α -terpineol for the high ozone and high air-exchange condition suggest reactivity towards ozone similar to that of d-limonene, in agreement with a recent determination (Wells, 2005). Its isomer, γ -terpineol, reacted at faster rates, similar to those of terpinolene. The α -terpineol results are not fully consistent among the experiments. The reproducibility of α -terpineol concentrations among samples collected in the same steady-state period also was low. These observations might be related to sorption of α -terpineol on chamber surfaces. The vapor pressures of the major constituents of the GPC-1 are relatively high (between 0.6 and 5 torr), while that of α -terpineol is roughly two orders of magnitude lower (0.023 torr) (Howard and Meylan, 1997). In the high ozone experiments (2A-2C), about 90% of the α -terpinene was consumed, compared with roughly 30-40% of the terpinolene and 15-20% of the d-limonene. For these three species, the apparent relative reactivity was roughly proportional to the product of their concentration and their reported reaction rates with ozone: 2×10^{-14} , 2×10^{-15} and 2×10^{-16} cm³ molecule⁻¹ s⁻¹, respectively (NIST, 2000). Ozone was substantially titrated by the excess of reactive VOCs in all experiments, so that the steady-state ozone levels in the chamber were no greater than 10% of those in the supply air. Consistent with expectations, Table 4.2 reveals that across all five ozone levels the observed extent of reaction depended more on the residual ozone level, which varied from < 1 ppb to ~ 25 ppb, than on the characteristic residence time, which varied from 0.3 to 1.0 h. The fractions of α -terpinene, terpinolene and d-limonene consumed in the five experiments are shown in Figure 4.1A.

In Table 4.3, we present data obtained from the reaction of the single volatile component of the orange oil-based degreaser (GPD-1), d-limonene, with ozone. Due to the large excess of d-limonene, only 20% reacted under high ozone conditions and 10% under low ozone conditions (see also Figure 4.1B). Conversely, more than 80% of the chamber ozone was consumed by reaction with d-limonene at the high air-exchange rate, and at the low air-exchange rate, the ozone level was almost completely depleted (95%).

The formulation of AFR-1 was the most complex among the studied products, with more than 30 components. A higher extent of sorption can be expected, owing to the fact that the vapor pressures of alcohols and esters in AFR-1 were significantly lower than those of the hydrocarbons contained in GPC-1 and GPD-1. Only five AFR-1 components exhibited significant reactivity toward ozone under these experimental conditions (Table 4.4). The two most reactive ingredients were linalool and d-limonene. The concentration of linalool was about twice that of d-limonene. Two different reports have placed the reaction rate of linalool with ozone at values that are similar to or slightly higher than that of d-limonene: $k < 3.16 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ and $k = 4.3 \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ (NIST, 2000). Their reaction rates with OH

are comparable, $k = 1.69 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for d-limonene and $k = 1.59 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for linalool (NIST, 2000). Here, we observed that linalool was more completely consumed, except for the moderate ozone condition (experiment 2K) in which d-limonene showed similar reactivity. Other reactive species in the air freshener were dihydromyrcenol, linalyl acetate and β -citronellol. While data on the bimolecular reaction rate of these terpenoids with ozone have not been published, our results suggest that the reaction rate of β -citronellol is comparable to that of linalool; the reaction rate of linalyl acetate is comparable to that of d-limonene; and dihydromyrcenol reacts at a slower rate. Experimental data are plotted in Figure 4.1C.

Appendix D contains detailed experimental data for these experiments. Tables D.1-D.31 report the measured concentrations of primary constituents and volatile oxidation products for each experimental sample. Figures D.1-D.23 display the particle sampling data from the SMPS and (where available) the OPC. Figures D.24-D.38 show the time dependent traces of ozone (and, in the case of D.38, of NO and NO₂ concentrations). Table D.32 reports time average ozone concentrations in the supply air and in the chamber.

4.3.2. Volatile oxidation products

Formaldehyde yields were similar for the reaction of GPC-1 and GPD-1 with ozone (in the range 20-30% for most conditions) and higher for AFR-1 (30-90%). The fact that several distinct terpene-based products led to high formaldehyde yields in the presence of ozone is an important result of this study, since formaldehyde is a toxic air contaminant with a low chronic reference exposure level (OEHHA, 2000). Although formaldehyde can be generated at various oxidation steps of many reactive VOCs (not only by ozonation but also through reaction with OH and other oxidant species) its principal chemical source in our system is the ozonation of d-limonene and, when present, linalool. Formaldehyde is produced as a primary carbonyl during ozonation of the terminal alkene group in d-limonene with a yield of $\phi_F = 0.10$ -0.19 (Atkinson and Arey, 2003). The contribution of that reaction to total formaldehyde production (X_{primary}) can be estimated for the GPD-1 data shown in Table 4.3, assuming that d-limonene is the single reactant and formaldehyde is the only carbonyl detected:

$$X_{\text{primary}} = \frac{\phi_F [O_3]_{\text{consumed}}}{[F]_{\text{produced}}} \quad (4-1)$$

Considering a lower limit for the formaldehyde yield of $\phi_F = 0.10$, the fraction of formaldehyde generated as a primary carbonyl in the ozonation of d-limonene from GPD-1 is $X_{\text{primary}} = 0.33$ for high O₃ and 3 h⁻¹, 0.40 for high O₃ and 1 h⁻¹, and 0.45 for moderate O₃ and 3 h⁻¹. Higher yields of formaldehyde measured in AFR-1 experiments are probably due to the presence of two reactive VOCs that generate formaldehyde as the primary carbonyl during ozonation (d-limonene and linalool). Similarly, the high acetone concentration measured for GPC-1 and AFR-1 likely originated in the primary ozonation of terpinolene and linalool, respectively. Background levels of these oxidation products before ozone addition were negligible except for acetone, present at 5 ppb in GPC-1.

Oxidation product yields reported for AFR-1 in Table 4.4 show a significant increase for experiment 2J conducted at 1 h⁻¹ (up to 90% for formaldehyde), suggesting an important effect owing to the longer residence time. A similar effect of residence time was not observed with

GPC-1 and GPD-1. Low vapor pressures can be expected for several AFR-1 components with GC retention times higher than those of GPC-1 components. Likely, such species sorb to surfaces and react on these surfaces with ozone in the chamber, thus contributing to the measured gas-phase concentration of oxidation products. While sorption of semivolatile components may be viewed as a limitation of the chamber method employed here, these results are of interest considering that similar processes would likely occur on indoor surfaces, possibly leading to analogous production of volatile oxidation products.

Considering the two volatile carboxylic acids detected, formic acid is an oxidation product of formaldehyde and is present at 30-80% of the formaldehyde level. Acetic acid is generated either in tertiary oxidation reactions or by hydrolysis of esters. Notably, background levels (i.e., without ozone) of acetic acid were high for AFR-1 (160-170 ppb), presumably due to partial hydrolysis of major fragrance components such as borneol acetate, linalyl acetate or phenylethyl acetate.

Glycolaldehyde is a biogenic VOC commonly measured together with terpenes and their oxidation products in environmental samples. Spaulding et al. (2003) identified glycolaldehyde among other oxygenated airborne chemicals collected at a pine plantation. Glycolaldehyde in our study is likely generated in the reaction of OH with partially oxidized terpenes. High yields of glycolaldehyde have been measured in the reaction of OH with biogenic VOCs such as 2-methyl-3-buten-2-ol, MBO, (~60%), allyl alcohol (47%), 1-penten-3-ol (87%) and Z-2-penten-1-ol (90%) (Reisen et al., 2003; Orlando et al., 2001; Alvarado et al., 1999). We did not obtain a positive identification for benzaldehyde, methylglyoxal or acrolein, but cannot rule out the presence of acrolein owing to the limitations of the DNPH carbonyl method.

4.3.3. Determination of hydroxyl radical concentrations

Figure 4.3 shows the OH concentrations derived for the three products as a function of the residual O₃ concentration in the chamber. These results are consistent in magnitude with those of Weschler and Shields (1997a) employing d-limonene and ozone mixtures, as well as with direct OH determinations in ozone/alkene mixtures using a laser-induced fluorescence method (Siese et al., 2001). The hydroxyl radical is short-lived, so that its concentration effectively depends on the dynamic balance between the rate of production and the rate of consumption by chemical reactions. These rates depend upon the concentrations of residual ozone and reactive VOCs. The pseudo-steady state balance can be approximated as:

$$[OH] = \frac{\sum_i k_i y_i [O_3][U_i]}{\sum_i h_i [U_i] + \sum_j h_j [S_j]} \quad (4-2)$$

where k_i is the bimolecular reaction rate between ozone and the unsaturated chemical U_i ; y_i is the corresponding OH formation yield; h_i and h_j are the bimolecular reaction rates for OH with unsaturated (U_i) and saturated (S_j) VOCs, respectively. High OH yields, between 0.38 and 0.74, have been reported for several of the studied terpenes (Aschmann et al., 2002). Typical k_i values are in the range 10^{-17} - 10^{-14} cm³ molecule⁻¹ s⁻¹, while h_i is in the range of 5×10^{-11} to 5×10^{-10} cm³ molecule⁻¹ s⁻¹ and h_j is in the range of 5×10^{-12} to 5×10^{-11} cm³ molecule⁻¹ s⁻¹ (NIST, 2000).

Equation 4-2 does not explicitly consider possible reactions of OH with secondary products from ozone-terpene reactions, which result in additional sinks for OH.

For cases in which the terpenoids are the most significant OH sinks (i.e., $\sum h_i[U_i] \gg \sum h_j[S_j]$), the steady-state OH radical concentration can be estimated in terms of only the concentration of ozone and the unsaturated VOCs (U_i), as follows:

$$[OH] = [O_3] \left(\frac{\sum_i k_i y_i [U_i]}{\sum_i h_i [U_i]} \right) \quad (4-3)$$

The assumed dominance of terpenoids as OH sinks appears to be a good approximation for our experiments with GPC-1 and GPD-1, but is less accurate for AFR-1, which contains substantial quantities of saturated species in addition to the terpenoids. In the case of GPD-1, which contains only one reactive unsaturated VOC (d-limonene), the approximate equation can be further simplified to be independent of the concentration of d-limonene:

$$[OH] = [O_3] \frac{k_i y_i}{h_i} \quad (4-4)$$

Figure 4.3 includes traces that correspond to the simplified models expressed by equations 4-3 and 4-4. The magnitude and trend agreement between these approximations and the experimentally derived OH levels indicates that the simple model equations capture the key features of OH chemistry in these experiments, particularly at high air-exchange rate. Model overestimates for the low air-exchange rate may be a consequence of the relatively higher concentrations of secondary oxidation products that would constitute an important additional sink for OH.

4.3.4 Secondary organic aerosol formation

Figure 4.4 shows the temporal evolution of the airborne particle volume concentration (top frame), the surface-area concentration (second frame), the number concentration (third frame), and the particle size distribution (bottom frame) for particles in the size range 8 - 412 nm, as measured with the SMPS in experiment 2K, in which AFR-1 volatile components were exposed to moderate ozone levels (63 ppb inlet concentration). Total number and volume concentrations were calculated by integrating the size distribution, and therefore do not account for particles that grew out of the measurement range of the SMPS. Qualitatively similar behavior was observed for all three products and experimental conditions, as can be seen in Appendix D, Figures D.1-D.23. A distinctive feature in all cases was the burst of ultrafine particle nucleation that occurred immediately upon ozone addition (indicated with the vertical dashed line at ~ 12:45 in Figure 4.4). Qualitatively, these results are consistent with recent reports of ultrafine particle formation and growth during the reaction of ozone with terpenes (Fan et al., 2005; Liu et al., 2004; Rohr et al., 2003). Remarkably, the production of ultrafine aerosol particles observed here is similar in its main features to nucleation events observed in the atmosphere (Kulmala et al., 2004; Kavouras et al., 1998) although the mixing ratio of terpenoids to ozone is significantly

higher in our experiments where ozone was virtually titrated by the large excess of the reactive compounds.

The total particle number concentrations, together with their corresponding aerosol masses (assuming density = 1 g/cm³) are reported in Table 4.6. We report values for the ultrafine fraction (< 0.1 μm diameter, PM_{0.1}), for the total particles measured with the SMPS (PM_{0.4}) and, when available, for total particles measured with the optical counter (PM_{1.1}). The designations of PM_{0.4} and PM_{1.1} are based on the largest particle sizes effectively measured by the SMPS and optical particle counter, respectively. Data were calculated at both peak conditions (~ 20-40 minutes after initial introduction of O₃ to the system) and at steady-state conditions (> 2 h or > 4 h after the start of O₃ addition for 3 h⁻¹ and 1 h⁻¹, respectively). Initial particle growth rates in the range 2 – 6 nm min⁻¹ are also reported in Table 4.6. The large number of particles measured at the peak of the burst was predominantly in the ultrafine fraction (diameter < 0.1 μm), although larger particles accounted for 70 – 80% of the peak particle mass under most experimental conditions. Peak particle concentrations scaled in proportion to the ozone and VOC consumed. When the amount of ozone and VOC that reacted at each experimental condition was similar for the three products, the amount of PM_{0.1} produced at the peak was largest for GPC-1, followed by GPD-1 and then AFR-1. Such differences can be rationalized by considering the combined product of the initial concentrations of the reactive VOCs (U_0) and their reaction rate with ozone (k_{O_3}), $\Sigma(U_0 k_{O_3})$, which varied in the same order (GPC-1 > GPD-1 > AFR-1). In addition, characteristics of the reaction byproducts are expected to affect the nucleation process. For example, the four reactive VOCs in GPC-1 and the single reactive terpene in GPD-1 (d-limonene) each have at least one endocyclic unsaturation that yields C₁₀ primary oxidation products upon ozonation. Conversely, of the four most reactive constituents in AFR-1, three react with ozone to fragment their carbon backbone, yielding products with nine or fewer carbon atoms, and therefore are less likely to nucleate or condense. For GPC-1 and GPD-1, experiments run at 1 h⁻¹ showed lower peak particle production than at 3 h⁻¹. For AFR-1, this trend was reversed.

At steady state, the ultrafine particle concentrations were markedly lower than the peak values, representing 30-70% of the total number concentrations and only 1-4% of the total mass concentrations for most experimental conditions. Following nucleation, aerosol-aging processes led to particle growth from the ultrafine to the accumulation mode (0.1-2 μm diameter). An estimation of aerosol particle yield (mass/mass) can be obtained from the ratio of the steady-state PM_{1.1} mass concentration (when available) to the sum of reacted VOC concentrations in each product. We so determined yields of 6-14% for GPC-1 components, 11-16% for GPD-1 (using PM_{0.4} values) and 4-6% for AFR-1. Yields determined for GPC-1 and GPD-1 are similar to those reported for ozone/d-limonene reactions (Weschler and Shields, 1999; Hoffmann et al., 1997). The relatively lower values for AFR-1 are consistent with reported observations for reactions of linalool with ozone (Hoffmann et al., 1997).

4.3.5. Surface application

For experiments 2L and 2M, a dry residue was obtained by means of applying a small quantity of the GPC-1 or the GPD-1 to a glass plate, then allowing it to dry under a flow of nitrogen to remove the volatile components. During subsequent exposure of the dry GPC-1 residue to ozone in the reaction chamber, initially high concentrations of α - and γ -terpineol (~ 1 ppm and 100 ppb, respectively) were measured at 15 and 100 min after introducing the plate. A measurement at 200 minutes showed declining values for the concentrations of these two

compounds (350 and 15 ppb respectively). During the first 3 h of ozone exposure, we observed the production of formaldehyde (with an average concentration during that period of 4.6 ppb), acetaldehyde (0.9 ppb), acetone (9.9 ppb) and glycolaldehyde (1.5 ppb). Figure D.35 in Appendix D shows the evolution of the ozone concentration in the chamber during experiment 2L. Figure 4.5 illustrates the time-dependent aerosol volume concentration (top frame), area concentration (second frame), number concentration (third frame), and particle size distribution (bottom frame) for experiment 2L. We observed a burst of ultrafine particle formation immediately following the introduction of the plate that was similar to the burst observed in the gas-phase experiments. The time evolution of the particle volume concentration mirrors closely the ozone trace (see Figure D.35 in Appendix D). Owing to the combined ozone exposure of the terpenoid reactants in both the gas phase and on the surface, we cannot discern the degree to which the observations are a result of homogeneous versus heterogeneous chemistry. However, when the same experiment was performed with dry residue from GPD-1, no primary VOCs were detected in the gas phase during the exposure to ozone, yet we did observe the formation of oxidation products during the initial 4 h of exposure (3.3 ppb formaldehyde, 2.8 ppb acetaldehyde and 11 ppb acetone). A burst of ultrafine particles and secondary aerosol growth similar to that shown in Figure 4.5 for GPC-1 was also observed when GPD-1 dry residue was exposed to ozone (see Appendix D, Figure D.20). These tests suggest that delayed desorption of reactive terpenoids of low volatility or the reaction of nonvolatile chemicals on the surface may constitute a source of secondary oxidation products and secondary organic aerosol.

4.3.6. *Effect of nitrogen dioxide*

Figure D.38 in Appendix D shows the concentration profiles of NO, NO₂ and O₃ in experiment 2O. Initial chamber concentrations in the absence of ozone were [NO₂] = 74 ppb and [NO] = 1.75 ppb. Average ozone concentration in the supply air was 139 ppb. When ozone was introduced in the chamber containing the GPC-1 components in combination with NO₂ and NO, the ozone steady-state concentration dropped to 20 ppb, and those of NO₂ and NO changed to 62 ppb and 0.73 ppb, respectively. Concentration of reactive VOCs measured before and after ozone addition, together with levels of stable oxidation products and their respective yields are reported in Table 4.5. While the degree of consumption of the main terpenoids did not change significantly relative to experiment 2B with only ozone, VOCs that were inert under ozone-only atmospheres exhibited more reactivity. Eucalyptol and p-cymene were consumed by about 8% in each case versus about 3% and 1%, respectively, without the nitrogen oxides. Yields of formaldehyde, acetone and carboxylic acids were slightly lower than in experiment 2B, but higher yields of acetaldehyde (11% vs. 1%) and glycolaldehyde (8% vs. 5%) were observed.

4.4. Room-Scale Experiments: Methods

4.4.1. *Introduction*

Many consumer cleaning products and air fresheners contain terpenoid compounds that volatilize during product application and use. Some of these compounds react rapidly with ozone to form secondary pollutants. Ozone enters indoor environments with outdoor air and typically is present indoors at levels that are 10 to 50% of concurrent outdoor levels (Weschler, 2000). Ozone also may be introduced by indoor sources including devices designed to generate ozone for claimed air purification (Boeniger, 1995), air cleaners generating ozone as a byproduct of ionization (Niu et al, 2001; Phillips et al., 1999; Zhao et al., 2005), and some photocopiers and printers (Leovic et al., 1986; Lee et al., 2001).

As reviewed in §2, ozone-terpenoid reactions produce carbonyl compounds such as formaldehyde and acetaldehyde, organic acids, other oxygenated intermediates, hydrogen peroxide, secondary organic aerosol, and hydroxyl radicals (OH). Subsequent reactions of OH with volatile organic compounds (VOCs) may generate additional formaldehyde, acetaldehyde and other products. While formaldehyde and acetaldehyde are important indoor toxicants, little is known about the toxicology of many terpenoid oxidation products.

Secondary pollutant formation from reactions involving ozone and terpenoid constituents of consumer products has been studied with various methods in an array of environments including a reactor tube (Wolkoff et al., 2000), small Teflon-lined chambers (Wainman et al., 2000 and §4.2-4.3 of this report), room-sized stainless-steel chambers (Fan et al., 2003; Liu et al., 2004; Sarwar et al., 2004), unoccupied offices (Weschler and Shields, 1997a; Weschler and Shields, 1999; Weschler and Shields, 2003), and residences (Long et al., 2000; Hubbard et al., 2005). Many of these studies used one or more pure compounds selected because they are common constituents of consumer products. A few recent studies have used actual consumer products to generate constituent mixtures (Liu et al., 2004; Sarwar et al., 2004). Information has been generated regarding formation of reaction products (Weschler and Shields, 1999; Li et al., 2002; Rohr et al., 2003), reactant consumption and product yield rates (§4.2-4.3), secondary pollutant levels under simulated but realistic conditions (Weschler and Shields, 1999; Long et al., 2000), and associations of secondary pollutants with specific consumer products (Sarwar et al., 2004). Data also have been generated for development and validation of mathematical models to simulate a wider range of events and to investigate potential population exposures (Sarwar et al., 2003; Liu et al., 2004). Despite this important recent progress, significant questions remain about the quantity of readily measured secondary pollutants formed for typical consumer use of products and about the relevance of laboratory results to potential consumer exposures in indoor environments.

In the work reported in §4.4-4.5 of this report, we attempt to bridge the gap between the laboratory and building environments by conducting experiments in a simulated residential room. Three off-the-shelf products — a general purpose cleaner, a degreaser and a plug-in scented oil air freshener — were applied in a realistic manner in a 50-m³ room-sized chamber constructed with standard building materials. For each product, experiments were conducted in the absence of ozone and with ozone introduced into the air supply at 120 ppb. Specifically, we studied the effects of ozone interactions with these products, with the intent of contributing toward the following goals: (1) broadly characterize ozone-terpenoid reactions for a range of consumer products and compounds; (2) quantify the formation of very volatile carbonyl reaction products; (3) estimate the levels of OH formed from ozone-terpenoid chemistry; and (4) characterize the formation of secondary organic aerosol.

4.4.2. Chamber, products, and application protocols

Reactions between ozone (O₃) and terpenoid constituents of consumer products were studied in a 50-m³ chamber designed to simulate a residential room. The chamber, products and most experimental protocols have been described in earlier sections of this report. Key points are reiterated here.

The chamber is finished with painted gypsum wallboard with sheet aluminum on the floor. The floor was partially covered with noncontiguous 3.9 m² and 7 m² sections of vinyl tiles. A table with laminate top (1.16 m²) was present. Ventilation supply air was drawn from outdoors and directed through a bed of activated carbon to remove VOCs and O₃. The chamber was

ventilated at $\sim 1 \text{ h}^{-1}$ at a positive pressure of $\sim 5 \text{ Pa}$ relative to the building. A household oscillating fan was operated at low or medium speed to facilitate mixing. The air-exchange rate (AER) was measured once or more during each experiment by monitoring the decay of injected SF_6 using a photoacoustic infrared analyzer (Model 1302, Brüel & Kjær). A high frequency corona discharge O_3 generator (OzoneLab GE30/FM100R, Yanco Industries, Ltd.) was connected to the supply air 1 m before the chamber inlet. Some experiments were run without supplied ozone, whereas in others, the generator provided O_3 at $\sim 120 \text{ ppb}$ in the supply air. Chamber air temperature and relative humidity were monitored in two locations (HOBO H8 Pro, Onset Computer Corp.).

Three widely used consumer products containing O_3 -reactive chemicals were employed: a general-purpose pine oil-based cleaner (GPC-1) packaged as a concentrated liquid; an orange oil-based degreaser (GPD-1) packaged as an aerosol foam; and a plug-in, scented-oil air freshener (AFR-1).

Table 4.7 summarizes for each experimental run the conditions and measured parameter results (AER, temperature, relative humidity). Each product was used in a realistic manner. In experiments involving GPD-1 (3A-3C), the product was sprayed onto a 0.11-m^2 section of aluminum sheet to simulate cleaning of a cooktop. After 1 min, the excess was wiped away with a paper towel and the towel and product container were removed from the chamber. For experiments utilizing GPC-1 (3D-3H), about 4 L of a solution of 1 part GPC-1 to 16 parts water was applied by sponge mop to the 3.9-m^2 section of composition flooring. The final two experiments (3J-3K) utilized the air freshener. The AFR-1 unit was plugged into an electrical outlet approximately two days before the start of experiment 3J. The device was initially set to low output (setting 1) then switched to high output (setting 3) at the end of experiment 3J. The AFR-1 container was weighed at several points including at the start and completion of each experiment. Product volatilization rate was observed not to vary in the manner expected by device setting (Table 4.7).

GPD-1 and GPC-1 experiments started with product application ($t = 0$). For each product, there were one or more experiments with O_3 and two control experiments without O_3 . The GPC-1 plus O_3 case was conducted in triplicate (experiments 3F-3H). Experiment 3I investigated floor mopping with water in the presence of O_3 , but without GPC-1. The floor was mopped with tap water at the end of each GPC-1 experiment to remove or at least reduce residue before the next experiment. When used, O_3 was introduced to the chamber at least 12 h prior to the start of GPD-1 and GPC-1 experiments. For AFR-1 experiments, VOC concentrations were already at steady state when the O_3 was introduced. Each AFR-1 experiment included measurement of pollutant concentrations over multiple hours before and after introduction of O_3 .

4.4.3. Air quality measurements

Chamber air was sampled to quantify concentrations of O_3 , specific VOCs, very volatile carbonyl compounds, and size-resolved particles. Analytical methods are summarized below.

Ozone was measured continuously with a UV analyzer (Model 400, Advanced Pollution Instrumentation, Inc.), calibrated to a primary standard for these experiments.

VOCs were collected onto sorbent tubes containing Tenax®-TA or Tenax backed by a carbonaceous sorbent. Tubes were thermally desorbed then analyzed by gas chromatography with mass selective detection (TD-GC/MS). VOC samples were collected over integrated periods (0-30, 30-90, 90-240, and 240-720 min) during all GPC-1 experiments and with greater time-resolution in some GPC-1 and all GPD-1 and AFR-1 experiments (3B-3C, 3E, 3F-3H, and 3J-

3K). Integrated samples were collected at $\sim 3.3 \text{ mL min}^{-1}$. Time-resolved samples were collected at $15\text{--}110 \text{ mL min}^{-1}$ over sampling periods of 1–20 min duration. Flow rates were measured during sampling. Samples were collected in duplicate with a subset analyzed to assess analytical precision. Targeted primary VOC analytes are listed in Tables 4.8 and 4.9.

Volatile organic compounds were collected without ozone scrubbers. This likely introduced a negative bias for some measurements, since terpenoids collected on Tenax may be degraded by ozone in sample air (Calogirou et al., 1996). The degree of degradation increases with ozone concentration, sampling time, and with the bimolecular reaction rate of the terpene with ozone. An MnO_2 -coated ozone scrubber has been found to reduce ozone-degradation of some terpenes; however, it also interfered with the collection of several compounds of interest in this study, including linalool. Several scrubber materials have been shown to be effective in removing ozone at 73–78 ppb without interfering with the sampling and analysis of ppb levels of five terpene hydrocarbons and five oxidation products. However, no terpene alcohols were considered in this study (Fick et al., 2001). Scrubbers were not used in the current study owing to concerns that they would retain (through sorption) the terpene alcohols in GPC-1 and the terpene alcohol, aldehyde, and ester constituents of AFR-1. Instead, when possible, samples were collected at low flow rates and over short durations to limit ozone-induced degradation.

Carbonyl compounds were collected on coated silica cartridges (P/N 047205, Waters Corp.). During experiments with O_3 , an ozone scrubber preceded each cartridge (P/N 054420, Waters Corp.). Cartridges were extracted with 2 mL acetonitrile. Extracts were analyzed by HPLC with UV diode-array detection at 360 nm following ASTM Method D 5197. Derivatives were quantified to determine concentrations of formaldehyde, acetaldehyde and acetone.

Size-resolved particle number concentrations were quantified using an optical particle counter (Lasair 1003, Particle Measuring Systems, Inc.). (The SMPS, which was used in the bench-scale experiments, was not available for the room-scale experiments.) The OPC was placed outside the chamber, and sample air was drawn at 0.03 L min^{-1} through 1.4 m of 1.7-mm ID copper tubing. The nominal size bins of the OPC are based on the instrument's response to polystyrene latex (PSL) calibration aerosol. The secondary organic aerosol generated in our experiments has different optical properties than PSL, necessitating adjustment of the bin boundaries. We used OPC bin boundaries reported by Hand and Kreidenweis (2001) that were determined by calibration of the same instrument model with oleic acid. This provided bin lower-size limits (aerodynamic diameters) of 0.15, 0.24, 0.36, 0.47, 0.62 and $0.89 \mu\text{m}$ for the first 6 bins; negligible counts were recorded in the two largest bins. These bin limits are different from those suggested by the instrument manufacturer, which are based on calibration with a polystyrene latex aerosol that has different optical properties. Some published studies have reported the data using the standard, manufacturer-recommended bins. There is some overlap in the sizes measured by the SMPS and OPC, which were both used in the small chamber experiments. Without the correction, the overlapping bins did not agree. With the correction, agreement was greatly improved; this confirmed the validity and value of using the correction.

The particle volume concentration in each bin was determined by multiplying the number concentration by $(\pi/6 \times \text{GMD}^3)$ where GMD is the geometric mean diameter of the bin. The mass distribution was estimated by multiplying the volume distribution by a particle density of 1 g cm^{-3} . This method likely underestimates the mass concentration, as organic aerosol density has been estimated to be approximately 1.2 g cm^{-3} (Turpin and Lim, 2001). The total particle mass concentration is described as $\text{PM}_{1.1}$, based on the upper boundary of $1.1 \mu\text{m}$ for the largest size bin sampled by the OPC. For the experiments reported here, the mass concentration of particles

between 1.1 μm and 2.5 μm in diameter is likely to be small, so that $\text{PM}_{1.1}$ and $\text{PM}_{2.5}$ are effectively equivalent. This inference is supported by the observation of negligible counts in the two largest size bins of the optical particle counter.

Hydroxyl radical concentrations were determined by an indirect method (Weschler and Shields, 1997a). Diffusion vials containing 1,3,5-trimethylbenzene (TMB) and perchloroethylene (PCE) were placed inside the chamber beneath the air inlet to provide relatively constant sources. With OH present, concentrations of TMB, but not PCE, are reduced by reaction with OH. Neither compound is depleted substantially by reaction with O_3 . TMB and PCE concentrations were quantified before and during experiments with O_3 and during experiment 3E without O_3 using the same sampling method as for the primary VOCs. OH was estimated from the measured decrement in the TMB/PCE ratio ($R_{T/P}$) as shown in equation 4-5. In this equation, λ is the AER, k is the bimolecular OH-TMB reaction rate constant ($1.44 \text{ ppb}^{-1} \text{ sec}^{-1}$), $R(0)$ is the ratio measured prior to $t = 0$, i.e. when no OH was present and $R_{T/P}(t)$ are ratios measured during an experiment.

$$[\text{OH}] = \left(\frac{\lambda}{k} \right) \left[\left(\frac{R(0)}{R(t)} \right) - 1 \right] \quad (4-5)$$

Hydroxyl radical concentrations were calculated using the TMB/PCE ratios rather than TMB concentrations directly because uncertainties related to sampling (e.g., pump flow rates), analysis (e.g., thermal desorption efficiency) and temperature-dependent variations in emissions are similar for TMB and PCE. Uncertainty in the calculated OH concentration is proportional to uncertainty in the TMB decrement ($[R(0)/R(t)] - 1$).

4.4.4. Data quality and uncertainty

Data quality procedures for the room-scale chemistry experiments were similar to those employed for the primary emissions experiments. VOC samples were collected prior to the start of each experiment to quantify chamber air concentrations of product constituents. The presence of measurable amounts of product constituent VOCs in the chamber one or more days after the end of the previous experiment indicates desorption of residual mass that had sorbed during previous experiments; these background concentrations were subtracted from those measured during all periods following introduction of cleaning products. VOC samples were collected in duplicate for all sampling periods; both collected samples were analyzed from two or more pairs in each experiment. Duplicates selected for analysis were drawn from various sampling periods across experiments to evaluate precision across a range of mass collected and gas-phase concentrations. In experiments involving use of GPC-1, VOC samples were collected at low flow rate over long, time-integrated periods and also at higher flow rate during more finely resolved sampling periods. Good agreement was observed between these sampling approaches when no ozone was present, supporting the robustness of the measurement technique. Very volatile carbonyl samples were always collected in duplicate and all samples were analyzed; values from the two samples were averaged together to obtain the concentration measurement reported for a given sample period. To investigate overall experimental reproducibility, several scenarios were evaluated with replication: mopping of floor with GPC-1 in the absence (experiments 3D-3E) and presence (experiments 3F-3H) of ozone, and use of the air freshener AFR-1 in the absence and presence of ozone (experiments 3J-3K).

4.5. Room-Scale Experiments: Results and Discussion

4.5.1. VOC constituents and chamber concentrations

GPC-1 and AFR-1 each contained mixtures of VOCs that were emitted during use, whereas GPD-1 only contained and emitted d-limonene. GPC-1 emissions were dominated by terpene hydrocarbons and alcohols (Table 4.8), while AFR-1 also emitted substantial quantities of terpene aldehydes and esters in addition to relatively unreactive, saturated VOCs (Table 4.9). A complete record of measured concentrations of the primary VOC components is presented in Appendix E, Tables E.1-E.13.

The time profiles of selected VOCs following application of GPD-1 and GPC-1 are shown in Figures 4.6 and 4.7, respectively. GPD-1 produced peak d-limonene concentrations in the chamber air of ~ 950 ppb in Exp. 3B and ~ 1400 ppb in Exp. 3C. (VOC data were not obtained in Exp. 3A). In Exp. 3B, conducted without ozone, d-limonene persisted at its peak level for approximately 90 min, suggesting ongoing emissions from the substrate. Mop application of GPC-1 yielded peak levels of 170-200 ppb for d-limonene, 70-200 ppb for terpinolene, and 110-130 ppb for α -terpineol, as measured at 10 min in Exps. 3E-3H (Figure 4.7). Unsaturated terpenoids totaled ~ 480-630 ppb during the first 30 min following GPC-1 use in Exps. 3D-3H (Table 4.8). With no O₃ present, most GPC-1 constituents initially declined at close to the measured air-exchange rate (Figure 4.8). Observed deviations from first-order decay of GPC-1 constituents and d-limonene from GPD-1 are consistent with expectations for reversible sorption (Singer et al., 2004).

The most abundant terpenoids in AFR-1 — d-limonene, dihydromyrcenol, β -citronellol, linalool, and linalyl acetate — were each present at steady levels of 1-11 ppb prior to introduction of O₃ (Table 4.9). Combined, unsaturated terpenoids were present at levels of 27 and 17 ppb for Exps. 3J and 3K.

Mopping the floor with water only (experiment 3I) produced no measured change in the levels of background VOCs in air.

The presence of ozone altered concentration profiles of several terpenoids, whereas saturated VOC concentrations were largely unaffected. The initial (0-1 h) first-order decay rates for α -terpinene, terpinolene, γ -terpineol, d-limonene, and a few other compounds were higher with ozone than without (Figure 4.8). Attributing this difference to reactive decay, VOC-O₃ reaction rate constants were estimated from the GPC-1 experiments by comparing initial decay rates calculated for Exps. 3G and 3H with those calculated for Exp. 3E. First-order decay rates for reactive compounds also were compared to the mean of nonreacting compounds in the same experiments to provide a second estimate of the decay rate owing to reaction. Bimolecular reaction rate constants were estimated using the mean ozone concentration over the 10-60 minute interval. Reaction rate constants determined in this way were within a factor of 2-3 of published values (NIST, 2000) for d-limonene, terpinolene, α -phellandrene, and γ -terpinene. Among compounds without published reaction rates, γ -terpineol and an unspecified terpene hydrocarbon eluting at 28.2 min were estimated to react with ozone at rates approximately 2-3 and 5-6 times, respectively, as fast as d-limonene (Figure 4.8). α -Terpineol concentrations initially did not decline more rapidly when ozone was present, contrary to expectations based on its published O₃ reaction rate (Wells, 2005). Delayed emission or sorption processes for terpene alcohols may have masked reaction-related α -terpineol decay. A similar deviation in the apparent reactivity of α -terpineol was observed in the bench-scale experiments. Since γ -terpineol likely sorbs at a rate

that is similar to α -terpineol, the reaction rate for the γ isomer likely is faster than estimated above.

Degradation on Tenax samplers is of minimal concern for these data owing to the high concentrations of terpene compounds (Figure 4.7 and Table 4.8), low ozone levels (Figure 4.9) and short (1-2 min) sampling intervals during this period.

Ozone continued to influence concentration patterns over the 12-h scale of each experiment with GPD-1 and GPC-1. The addition of ozone extended the period over which d-limonene decayed in roughly a first-order process to about 8 h for GPD-1 (Figure 4.6) and 6 h for GPC-1 (Figure 4.7). A similar pattern was observed for α -terpineol and terpinolene; the latter decayed faster (Figure 4.7), consistent with its faster reaction rate with ozone. Concentration patterns of p-cymene, eucalyptol, and even some terpenes (e.g., α -pinene and camphene) were largely unaffected by the presence of ozone.

In the AFR-1 experiments, VOC emissions from the source continued at approximately steady rates while ozone was introduced, as confirmed by the small measured change in the steady-state concentrations of benzyl acetate and bornyl acetate after ozone was added (Table 4.9). Expected steady-state concentrations of ozone-reactive VOCs in the presence of ozone were calculated by mass balance, using the mass emission rate inferred before ozone was added (adjusted for the change in AFR-1 volatilization rate, as shown in the third column of Table 4.7), and considering removal by ventilation and reaction. Removal by reaction was estimated using the measured ozone concentration and the published bimolecular reaction rates for terpene-ozone reactions. Table 4.9 indicates that the 47 ppb of ozone in the chamber air at steady state (Exp. 3J) is expected to lower the gas-phase concentrations of d-limonene and β -citronellol by about half, and concentrations of linalool and linalyl acetate by about two-thirds.

4.5.2. Ozone concentrations and reactions

Ozone concentration profiles are shown in Figure 4.9 for selected experiments and in Appendix E, Figures E.12-E.22 for the full set. Prior to the introduction of cleaning products, O_3 concentrations in the chamber were steady at about one-half the level in the supply air. This relationship was used to calculate, by material balance, the rate of O_3 deposition and decomposition on surfaces in the chamber. The 1 h^{-1} O_3 loss rate is at the low end of those measured in residences (Lee et al., 1999), similar to that measured in a telephone switching office (Weschler et al., 1994), and consistent with values expected for an unfurnished room.

Ozone levels dropped rapidly with application of the cleaning products. Concentrations decreased to the minimum observed levels within 10 min of GPD-1 use in Exp. 3C (upper left of Figure 4.9) and within 13 min of GPC-1 use in Exp. 3H (upper right of Figure 4.9). Minimum O_3 concentrations were steady at ~ 4 ppb from 10 to 60 min after GPD-1 use in Exp. 3C and at ~ 6 ppb from 10 to 40 min after GPC-1 use in Exp. 3H. In Exps. 3F-3G, minimum concentrations were 7.5 ppb during the period 20 to 40 min after product use. Ozone concentrations increased gradually beginning about 1 h after the cleaning application. Concentrations remained below the steady-state level for 10-12 h following product application, indicating continued consumption by reaction with residual cleaning product constituents. In Exp. 3I, ozone concentrations in chamber air started to decline during the hour before the floor was mopped with water and reached a low of about 44 ppb at 12 min after mopping (Figure 4.9, bottom right). No similar decline in ozone was observed prior to the start of mopping in Exps. 3F-3H, despite similar preparation activities. The sharper decline following the start of Exp. 3I may in part be related to

an increase in the ozone decomposition rate on surfaces associated with an increased relative humidity in the chamber (Grøntoft et al., 2004) caused by mopping.

The relationship between the quasi-steady O₃ concentrations in the chamber during the first hour and concentrations in the supply air was used to calculate, by material balance, the rate of O₃ consumption by reaction following product use. Steady concentrations of 4, 6, and 7.5 ppb correspond to total O₃ consumption rates of 30, 20, and 16 h⁻¹, respectively. Since deposition to surfaces (1 h⁻¹) is much slower, most O₃ consumption was due to reaction with cleaning product constituents, either in the gas phase, or on surfaces. VOC concentrations were combined with known or estimated O₃ reaction rates to calculate O₃ consumption attributable to gas-phase reactions and to predict steady O₃ concentrations. For example, in experiment 3C (GPD-1), the average gas-phase concentration of d-limonene over the 10-60 min interval was 1070 ppb. Combining this with the d-limonene-O₃ reaction rate of 5.2×10^{-6} ppb⁻¹ s⁻¹ (NIST, 2000) and the AER of 1 h⁻¹ yielded a predicted O₃ consumption rate (reaction + deposition) of 21 h⁻¹ and a steady concentration of 5.5 ppb. A similar calculation for experiment 3H (GPC-1) yielded the following estimates of O₃ consumption rates by the five predominant terpenoids, based on their mean concentrations over the 10-40 min interval: terpinolene, 17 h⁻¹; α-terpinene, 3.6 h⁻¹; d-limonene, 3.0 h⁻¹; α-terpineol, 2.1 h⁻¹; and α-phellandrene, 2.1 h⁻¹. An O₃ concentration of 4 ppb was predicted based on the total consumption rate of 28 h⁻¹. Thus, measured O₃ concentrations were consistent with predictions based on homogeneous reaction rates.

Over the course of the first hour following cleaning product application, the total mass of O₃ consumed was ~ 18-19 mg, which includes most of the 6.5 mg present initially and about 95% of the 13 mg entering with supply air over this period.

In AFR-1 experiments, O₃ was introduced into the chamber already containing reactive and non-reactive VOCs. AFR-1 use in the absence of O₃ produced reactive VOC concentrations in air that were 1.5 to 2 orders of magnitude lower than in experiments with cleaning products. The AFR-1 source continued to emit throughout the measurement periods. After approximately 3 h in Exps. 3J and 3K, the chamber O₃ concentrations were steady at 81% and 87%, respectively, of the 57 ppb expected for the inlet O₃ concentration of 114 ppb (Exp. 3K, Figure 4.9, bottom left). The total ozone loss rates from chamber air were determined by material balance to be 2.45 h⁻¹ for Exp. 3J and 2.31 h⁻¹ for Exp. 3K. These rates include air-exchange (1 h⁻¹), heterogeneous decomposition and homogeneous reaction. The ozone consumption and secondary pollutant formation potential of AFR-1 has three possible components: (1) constituents already present in the air when O₃ is introduced, (2) continuously emitted constituents, and (3) a reservoir of constituents sorbed to material surfaces. Compounds already in the air when ozone is introduced should impact ozone consumption only over the time scale of air exchange, i.e. for a few hours. Steady-state levels depend on the other two factors. Their relative importance was assessed by calculating ozone consumption associated with homogeneous reactions with VOCs emitted by AFR-1. This analysis used the calculated steady-state concentrations of VOCs in the presence of ozone (Table 4.9, column 5) and published or estimated rate constants for reaction with ozone. The following published rate constants were used: d-limonene 5.2×10^{-6} ppb⁻¹ s⁻¹ (NIST, 2000); linalool 1.1×10^{-5} ppb⁻¹ s⁻¹ (NIST, 2000); β-citronellol 5.9×10^{-6} ppb⁻¹ s⁻¹ (Ham et al., 2006). Based on the results presented earlier in this section, we estimated an ozone reaction rate for linalyl acetate that is twice the value for d-limonene. The reaction rate between ozone and dihydromyrcenol was estimated at 3×10^{-8} ppb⁻¹ s⁻¹ (JR Wells, personal communication). The results of this calculation, shown in Table 4.9 for Exp. 3J, suggest that homogeneous reaction with identified AFR-1 constituents accounted for

ozone consumption rates of 0.19 h^{-1} in Exp. 3J and 0.11 h^{-1} in Exp. 3K. The remaining ozone consumption, 1.26 h^{-1} in Exp. 3J and 1.20 h^{-1} in Exp. 3K, is assumed to result from heterogeneous reactions. We suspect that these rates are higher than the surface decomposition rate without AFR-1 (1.0 h^{-1}) because of ozone reaction with AFR-1 constituents sorbed to room materials. Note that this result was obtained for an unfurnished chamber. Residential rooms and offices contain larger quantities of material surfaces and more plush materials that would be expected to increase the concentration of sorbed VOC mass. Heterogeneous reactions between ozone and AFR-1 constituents could thus be more important in residences than in our chamber experiments.

4.5.3. OH radical concentrations and reactions

OH concentrations calculated from the measured TMB/PCE ratios are summarized in Table 4.10. Additional details of the measured TMB/PCE concentrations are presented in Appendix E, Tables E.14-E.20. The results indicate significant OH concentrations persisting for 10-12 hours following a single cleaning event; this finding is consistent with the observation that measurable O_3 consumption persists over the same period. Indeed, in the case of GPD-1, the measured OH concentrations were higher during the periods from 2-12 or 6-10 hours than during the first 2 hours. Although not necessarily intuitive, these results are consistent with predictions of a model that captures the essential features of the system, as described in §4.3. d-Limonene, through reaction with O_3 , is both a source of OH and at the same time a sink for OH. As the limonene concentration in the GPD-1 experiment decreases, the O_3 concentration increases. The rate of OH production does not decline as fast as the rate of OH removal, with the net effect that the OH concentration is expected to peak several hours after the end of the cleaning event.

The OH concentrations estimated during constant AFR-1 operation were within a factor of two of those determined for cleaning product use. OH concentrations resulting from the present experiments were similar to those reported in an office in which ozone and d-limonene were added to achieve steady-state levels of ~ 110 ppb and ~ 60 ppb respectively (Weschler and Shields, 1997a). In the bench-scale experiments described in §4.2-4.3, we observed a wider range of OH concentrations that were centered at the same order of magnitude as the results from these simulated product use experiments.

It should be noted that the OH concentrations reported in Table 4.10 are higher than would be anticipated in actual indoor settings that have higher concentrations of background VOCs; such VOCs can be significant OH sinks, contributing to its overall scavenging.

4.5.4 Secondary pollutants: Very volatile carbonyls

As summarized in Table 4.11, production of formaldehyde was associated with the use of each product in the presence of O_3 . (See Appendix E, Table E.21 for additional details). Relative to experiments without O_3 , product use in the presence of O_3 led to increased formaldehyde concentrations of 9-16 ppb over the 0-4 h period after cleaning product application and 5-10 ppb over the 4-12 h period after application. Air freshener use with O_3 resulted in a ~ 6 ppb increase in formaldehyde concentration over the 2-5 h period after O_3 addition. Here, the condition appeared to approximate steady state, based on stable concentrations of O_3 and reactive VOCs. Acetone was also produced during the use of GPC-1 and AFR-1 in the presence of O_3 . For GPC-1, the initial increase in acetone level averaged over the 0-4 h period was 29 ppb. There was no indication of acetaldehyde production in these experiments. The production of formaldehyde and acetone, but not acetaldehyde, is consistent with the location of the unsaturated carbon-carbon

bonds in the reactive VOCs identified as constituents of these products. These results are semi-quantitatively similar to those reported in the bench-scale chamber experiments.

4.5.5. Secondary pollutants: Particle number and mass concentrations

Shortly after the introduction of GPD-1 and GPC-1, particle number concentration as measured by the optical particle counter was observed to increase in several size-ranges, with the largest increase occurring in the smallest measured range (0.15-0.24 μm). For GPD-1, particle growth over time shifted through progressively larger size ranges in a particle growth wave similar to those reported previously (Sarwar et al., 2004). GPC-1 use produced substantial particle growth only up to the 0.24-0.36 μm particle size bin. Particle number concentrations were elevated for 8-10 h for GPD-1 and ~ 6 h for GPC-1. The increase in particle number concentrations resulting from O_3 introduction during AFR-1 use was small relative to increases in experiments with GPD-1 and GPC-1.

The evolution of calculated fine particle mass is presented for three experiments (3C, 3G, and 3J) in Figure 4.10. For each cleaning product experiment, mean $\text{PM}_{1.1}$ concentrations were calculated over a 12-h period starting with product use; for AFR-1 experiments, mean $\text{PM}_{1.1}$ concentrations were calculated at steady levels before and after O_3 addition. These results are summarized in Table 4.12. Peak $\text{PM}_{1.1}$ concentrations were estimated to be $\sim 275 \mu\text{g m}^{-3}$ for GPD-1 and $\sim 135 \mu\text{g m}^{-3}$ for GPC-1. The 12-h mean fine-particle mass concentration increased by almost $90 \mu\text{g m}^{-3}$ for GPD-1 in the presence of O_3 and by $30\text{-}35 \mu\text{g m}^{-3}$ for GPC-1 in the presence of O_3 , as compared with the experiments without O_3 . These are substantial increases, given that the State of California standard for suspended particulate matter in ambient air is $50 \mu\text{g m}^{-3}$ on a 24-h average basis (PM_{10}) and $12 \mu\text{g m}^{-3}$ on an annual average basis ($\text{PM}_{2.5}$) (<http://www.arb.ca.gov/research/aaqs/caaqs/pm/pm.htm>).

The difference between secondary PM levels generated by O_3 exposure of GPD-1 versus GPC-1 reflects in part the growth of particles associated with GPD-1 to larger sizes relative to the particles formed from the oxidation of GPC-1 constituents. Ultrafine particle formation and growth resulting from O_3 reactions with the same cleaning products was observed in the bench-scale experiments described in §4.3-4.4. In contrast to the cleaning products, use of the AFR-1 in the presence of O_3 produced much smaller quantities of $\text{PM}_{1.1}$ ($2\text{-}5 \mu\text{g m}^{-3}$ increases, as indicated in Table 4.12).

Particle concentrations measured in these simulated product use experiments are generally similar to those reported in previous experiments conducted in large chambers or indoor environments (Long et al., 2000; Fan et al., 2003; Sarwar et al., 2004; Liu et al., 2004). More detailed information about aerosol measurements in our experiments can be found in Appendix E, Figures E.1-E.11.

4.5.6. Relevance to real-world scenarios and exposures

The protocols and conditions employed in this study were designed to be relevant to product use under typical real-world conditions. The 114-120 ppb of O_3 in the chamber inlet air, which is analogous to outdoor air entering a home, is within a factor of 2 of outdoor levels commonly occurring during warm, sunny conditions in US urban areas (USEPA, 2004b). The steady-state level of O_3 in the chamber is within the range of reported indoor values (Weschler, 2000), albeit at the higher end of this range.

The use of a chamber finished with painted wallboard allowed for sorption to a material that is ubiquitous in US indoor environments. Owing to the use of appropriately scaled cleaning

surface area to room air volume ratios and realistic application protocols, concentrations measured at the start of GPD-1 and GPC-1 experiments are expected to be relevant to product use in residences. The AER of 1 h^{-1} corresponds to the 80th percentile of an empirical distribution reported for US detached residences across all seasons (Murray and Burmaster, 1995); use of a higher than average value may be especially appropriate during cleaning events with windows opened. Use of a single AFR-1 device in the 50-m^3 chamber approximates scenarios in which multiple plug-in devices are used in a larger residence or a single device is used in a small apartment. It is interesting to note that, at this moderate rate of AFR-1 use, concentrations of reactive terpenoids in air were 1.5-2 orders of magnitude lower than those resulting from cleaning product use.

The increase in formaldehyde concentrations resulting from cleaning product or air freshener use may be evaluated in the context of established exposure guidelines. The State of California has established non-cancer reference exposure limits (RELs) of 68 ppb for acute (1 hour) and 2.2 ppb for chronic (10 years or more) exposures to formaldehyde (OEHHA, 2000), and an interim 8-h REL of 27 ppb based on the acute value (CARB, 2005b). California's no significant risk level for cancer is a 70-year inhalation intake rate of $40 \mu\text{g d}^{-1}$ (OEHHA, 2005). Formaldehyde increments of 6-12 ppb averaged over 12 h following use of a single cleaning product would constitute about 20-40% of the 8-h REL that was set to protect against irritancy. When this is combined with other indoor sources and with formaldehyde transported from outdoors, such increments may increase the frequency or extent of exceedences of the 8-h REL. Chronic exposures scale with the frequency of use. A single event at the formaldehyde levels found in our study would contribute roughly 20-50% of the weekly average exposure or intake corresponding to California's noncancer and cancer chronic exposure guidelines. More frequent cleaning activity — e.g., by professional house cleaners or fastidious homemakers — could lead to exposures that exceed the chronic guidelines on a weekly averaged basis. On the other hand, the levels of secondary pollutants from ozone-terpene chemistry are expected to correlate with indoor ozone levels, whether from ambient air or indoor sources. A thorough chronic exposure assessment would need to consider the influence of the spatial variability, and the diurnal and seasonal cycles of ambient ozone on secondary pollutant formation.

Table 4.12 shows that use of certain cleaning products in the presence of O_3 can cause substantial incremental exposure to fine particulate matter. Epidemiological studies have shown associations between increases in ambient fine-particle concentrations and mortality and morbidity (Pope et al., 2002). However, the relative toxicity of particles collected at outdoor monitoring stations versus secondary organic aerosol derived from ozone-terpene reactions has yet to be determined.

4.6. Conclusions

The laboratory investigation described in §4.2-4.3 demonstrates the potential impact of ozone-initiated chemistry involving constituents of common household products. Such impact includes the formation of secondary gaseous pollutants and particles. Widespread use of cleaning products and air fresheners in close proximity to humans suggests that the reactive chemistry may contribute significantly to indoor exposure to certain toxic air contaminants and to ultrafine and fine-mode secondary organic aerosol. The simulated-use investigation described in §4.4-4.5 documents that the secondary pollutants observed in the bench-scale chamber experiments also can be observed in circumstances that mimic real-life conditions.

Overall, this study demonstrates that use of cleaning products that contain terpenoids, combined with ambient O₃ entering the indoor environment at concentrations common in urban areas, produce substantial levels of secondary air pollutants. Specifically, both formaldehyde and fine particulate mass are generated in quantities that, combined with other common sources, may result in exposures exceeding relevant health-based standards and guidelines. Also, both O₃ and OH may generate “stealth” products that cannot be measured with the methods employed here, but nevertheless raise potential health concerns (Weschler and Shields, 1997b; Wolkoff et al., 1997; Carslaw, 2003; Weschler 2004a; Weschler 2004b).

Sorption processes associated with material surfaces can delay the removal of volatile product constituents by ventilation and extend emissions. Thus, even if a cleaning event is performed in advance of elevated ambient O₃, terpenoid constituents of the product may be present at high enough levels to initiate indoor chemistry when ambient O₃ levels increase. Air fresheners emit terpenoids at rates that produce substantially lower concentrations than those that persist just after use of a cleaning product containing these compounds. However, since air fresheners represent a constant source, secondary pollutants formed when their constituent VOCs react with O₃ represent more of a chronic exposure concern.

Table 4.13 provides a concise summary of the specific findings reported in §4.

Table 4.1. Summary of experimental conditions for investigating reactive chemistry between ozone and two cleaning products (GPC-1 and GPD-1) and one air freshener (AFR-1) in a bench-scale chamber.

Expt.	Product	[O ₃] (ppb) ^a	ACH (h ⁻¹) ^b	Residue? ^c	NO ₂ ? ^c	Data tables ^d	SMPS figure ^e	OPC figure ^e
2A	GPC-1	253	3			4.2, D.1-D.2	D.1	D.2
2B	GPC-1	131	3			4.2, D.3-D.8	D.3	D.4
2C	GPC-1	130	1			4.2, D.9-D.10	D.5	
2D	GPC-1	65	3			4.2, D.11-D.12	D.6	
2E	GPC-1	29	3			4.2, D.13-D.14	D.7	D.8
2F	GPD-1	137	3			4.3, D.15-D.16	D.9	
2G	GPD-1	136	1			4.3, D.17-D.18	D.10	
2H	GPD-1	61	3			4.3, D.19-D.20	D.11	
2I	AFR-1	126	3			4.4, D.21-D.22	D.12	D.13
2J	AFR-1	127	1			4.4, D.23-D.24	D.14	D.15
2K	AFR-1	63	3			4.4, D.25-D.26	D.16	D.17
2L	GPC-1	118	1	✓		D.27-D.28	D.18	D.19
2M	GPD-1	114	1	✓			D.20	
2N	AFR-1	122	1	✓		D.29	D.21	
2O	GPC-1	139	3		✓	4.5, D.30-D.31	D.22	D.23

^a Ozone levels in supply air.

^b Nominal air-exchange rate (ACH), controlled by varying ventilation rate.

^c A “✓” indicates that the parameter was present in that particular experiment; see text.

^d Primary tables for presentation of gaseous species concentration data

^e Primary figures for presentation of particulate matter data

Table 4.2. Reaction of ozone with components of pine oil-based cleaner (GPC-1) in bench-scale chamber experiments.

	Expt. 2A (3 ach)		Expt. 2B (3 ach)		Expt. 2C (1 ach)		Expt. 2D (3 ach)		Expt. 2E (3 ach)	
species	C (ppb)	reacted (%)	C (ppb)	reacted (%)	C (ppb)	reacted (%)	C (ppb)	reacted (%)	C (ppb)	reacted (%)
ozone ^a	253 ± 4	90 ± 10	131 ± 4	90 ± 7	130±13	94 ± 15	65 ± 2	97 ± 11	29 ± 1	100 ± 58
VOC components ^b										
α-terpinene	22.5 ± 1	96 ± 2	25 ± 1	92 ± 3	25 ± 2	89 ± 4	24 ± 2	72 ± 7	16 ± 1	67 ± 2
d-limonene	204 ± 6	25 ± 2	219 ± 2	17 ± 0.7	229 ± 6	15 ± 2	206 ± 5	1.2 ± 3.8	202 ± 3	4 ± 1
p-cymene	40 ± 2	-3 ± 3	41 ± 0.5	1.2 ± 1.3	42 ± 2	1.6 ± 3.1	37 ± 2	-4.4 ± 5.2	49 ± 1	0 ± 2
eucalyptol	53 ± 2	-3 ± 2	58 ± 0.4	3.3 ± 0.5	60 ± 2	2.6 ± 2.5	46 ± 9	-19 ± 13	53 ± 1	-2 ± 2
terpinolene	240 ± 8	66 ± 4	266±12	43 ± 3	266±14	33 ± 4	236±32	8 ± 12	130 ± 3	12 ± 2
α-terpineol	146 ± 3	23 ± 2	149 ± 4	14 ± 2	104 ± 3	-9 ± 2	154±25	-2 ± 11	104 ± 18	-18 ± 13
γ-terpineol	18 ± 2	66 ± 5	13 ± 2	41 ± 8	12 ± 1	19 ± 3	19 ± 3	16 ± 12	11 ± 2	-4 ± 14
volatile oxidation products ^c										
	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)	C (ppb)	yield (%)
formaldehyde	59 ± 1	26 ± 1	34.5 ± 1	28 ± 1	35 ± 0.5	27 ± 0.4	13 ± 0.5	20 ± 1	4.6 ± 0.6	16 ± 2
acetaldehyde	4.4±0.8	1.9 ± 0.3	2.2±2.3	1.0 ± 1.3	2.2±1.2	1.0 ± 0.5	1.6±1.1	0.8 ± 0.6	nd ^d	
acetone	123 ± 3	54 ± 1	81 ± 5	66 ± 4	83 ± 3	63 ± 2	29 ± 1	45 ± 2	7.5 ± 4.7	26 ± 16
glycolaldehyde	17 ± 2	7.4 ± 0.7	11 ± 0.3	4.9 ± 0.1	12 ± 0.4	5.2 ± 0.2	5.4±0.3	2.6 ± 0.1	3.5 ± 0.1	12 ± 1
formic acid	40 ± 9	17 ± 4	26.5 ± 4	22 ± 4	12 ± 5	9 ± 4	10 ± 15	15 ± 23	4 ± 15	13 ± 26
acetic acid	55 ± 9	24 ± 4	38 ± 7	31 ± 6	22 ± 12	17 ± 9	3 ± 22	5 ± 33	nd ^d	

Concentrations (C) are reported for these conditions: ^a ozone level in reaction chamber without cleaning product; ^b VOC components in reaction chamber without ozone; and ^c volatile oxidation products in reaction chamber with both ozone and VOC components. ^d nd = not detected. Indicated variability represents ± standard deviation from duplicate determinations.

Table 4.3. Reaction of ozone with d-limonene from orange oil-based degreaser (GPD-1) in bench-scale chamber experiments.

	Expt. 2F (3 ach)		Expt. 2G (1 ach)		Expt. 2H (3 ach)	
species	<i>C</i> (ppb)	reacted (%)	<i>C</i> (ppb)	reacted (%)	<i>C</i> (ppb)	reacted (%)
ozone ^a	137 ± 9	85 ± 6	136 ± 7	95 ± 17	61 ± 2	82 ± 12
VOC components ^b						
d-limonene	643 ± 20	19 ± 2	738 ± 14	20 ± 6	586 ± 4	9.9 ± 1.1
volatile oxidation products ^c						
	<i>C</i> (ppb)	yield (%)	<i>C</i> (ppb)	yield (%)	<i>C</i> (ppb)	yield (%)
formaldehyde	32 ± 0.3	28 ± 0.2	36 ± 1	28 ± 1	13 ± 0.5	26 ± 1
formic acid	14 ± 5	12 ± 4	19 ± 12	15 ± 9	4 ± 7	7 ± 15
acetic acid	20 ± 10	17 ± 8	31 ± 22	24 ± 18	8 ± 40	16 ± 81

Concentrations (*C*) are reported for these conditions: ^a ozone level in reaction chamber without cleaning product; ^b VOC components in reaction chamber without ozone; and ^c volatile oxidation products in reaction chamber with both ozone and VOC components. Indicated variability represents ± standard deviation from duplicate determinations.

Table 4.4. Reaction of ozone with air freshener components (AFR-1) in bench-scale experiments.

	Expt. 2I (3 ach)		Expt. 2J (1 ach)		Expt. 2K (3 ach)	
species	<i>C</i> (ppb)	reacted (%)	<i>C</i> (ppb)	reacted (%)	<i>C</i> (ppb)	reacted (%)
ozone ^a	126 ± 6	86 ± 15	127 ± 5	97 ± 67	63 ± 0.5	89 ± 11
VOC components ^b						
d-limonene	121 ± 2	29 ± 2	165 ± 11	29 ± 7	108 ± 3	22 ± 3
linalool	176 ± 3	36 ± 2	247 ± 17	41 ± 6	170 ± 4	20 ± 3
linalyl acetate	66 ± 7	22 ± 9	88 ± 8	25 ± 12	57 ± 3	19 ± 24
dihydromyrcenol	241 ± 3	4.5 ± 1.4	335 ± 23	6 ± 11	242 ± 6	7 ± 3
β-citronellol	19 ± 1	40 ± 2	24 ± 2	40 ± 7	19 ± 1	25 ± 5
volatile oxidation products ^c						
	<i>C</i> (ppb)	yield (%)	<i>C</i> (ppb)	yield (%)	<i>C</i> (ppb)	yield (%)
formaldehyde	41 ± 0.4	38 ± 0.4	111 ± 2	90 ± 1	16 ± 2	29 ± 4
acetaldehyde	nd ^d		13 ± 0.4	11 ± 0.4	nd ^d	
acetone	41 ± 5	38 ± 52	95 ± 1	77 ± 1	14 ± 0.6	25 ± 1
glycolaldehyde	13 ± 0.3	12 ± 0.2	33 ± 0.5	27 ± 0.4	7 ± 0.3	13 ± 0.5
formic acid	24 ± 6	22 ± 6	68	55	14 ± 6	25 ± 11
acetic acid	36 ± 23	34 ± 22	84	68	nd ^d	

Concentrations (*C*) are reported for these conditions: ^a ozone level in reaction chamber without air freshener; ^b VOC components in reaction chamber without ozone; and ^c volatile oxidation products in reaction chamber with both ozone and VOC components. ^dnd = not detected. Indicated variability represents ± standard deviation from duplicate determinations.

Table 4.5. Reaction of ozone with components of pine oil-based cleaner (GPC-1) in bench-scale chamber experiments, with and without the presence of NO₂.

	Expt. 2B (3 ach)		Expt. 2O (3 ach)	
species	C (ppb)	reacted (%)	C (ppb)	reacted (%)
ozone ^a	131 ± 4	90 ± 7	139 ± 2	94 ± 8
VOC components ^b				
α-terpinene	25 ± 1	92 ± 3	22 ± 2	90 ± 10
d-limonene	219 ± 2	17 ± 0.7	231 ± 5	20 ± 3
p-cymene	41 ± 0.5	1.2 ± 1.3	47 ± 1	8 ± 4
eucalyptol	58 ± 0.4	3.3 ± 0.5	61 ± 1	8 ± 3
terpinolene	266 ± 12	43 ± 3	261 ± 14	41 ± 8
α-terpineol	149 ± 4	14 ± 2	174 ± 3	7 ± 3
γ-terpineol	13 ± 2	41 ± 8	21 ± 1	41 ± 4
volatile oxidation products ^c				
species	C (ppb)	yield (%)	C (ppb)	yield (%)
formaldehyde	34.5 ± 1	28 ± 1	29 ± 1	21 ± 1
acetaldehyde	2.2 ± 2.3	1.0 ± 1.3	15 ± 1	11 ± 1
acetone	81 ± 5	66 ± 4	70 ± 4	50 ± 4
glycolaldehyde	11 ± 0.3	4.9 ± 0.1	11 ± 1	8 ± 1
formic acid	26.5 ± 4	22 ± 4	12 ± 10	9 ± 7
acetic acid	38 ± 7	31 ± 6	38 ± 7	27 ± 6

Concentrations (C) are reported for these conditions: ^a ozone level in reaction chamber without cleaning product; ^b VOC components in reaction chamber without ozone; and ^c volatile oxidation products in reaction chamber with both ozone and VOC components. ^d nd = not detected. Indicated variability represents ± standard deviation from duplicate determinations.

Table 4.6. Data summary for secondary organic aerosol formation in bench-scale chamber experiments with two cleaning products (GPC-1 and GPD-1) and one air freshener (AFR-1).

experiment	initial growth rate (nm min ⁻¹)	peak concentrations				steady-state concentrations				
		number (10 ⁵ cm ⁻³)	mass ^a (μg m ⁻³)			number (10 ⁵ cm ⁻³)		mass ^a (μg m ⁻³)		
		PM _{0.1}	PM _{0.1}	PM _{0.4}	PM _{1.1}	PM _{0.1}	PM _{0.4}	PM _{0.1}	PM _{0.4}	PM _{1.1}
pine oil-based cleaner (GPC-1)										
2A	4.5	3.6	72	306	306	0.06	0.16	1.0	107	215
2B	3.8	2.4	46	162	162	0.04	0.11	0.7	67	115
2C	1.6	1.6	27	102	na	0.05	0.14	1.0	68	na
2D	2.6	1.2	19	57	na	0.13	0.24	1.4	50	na
2E	2.6	0.5	8	12	12	0.07	0.1	1.0	11	11
2O		1.8		146			0.14		64	
orange-oil based degreaser (GPD-1)										
2F	5.8	1.4	37	229	na	0.06	0.18	1.2	105	na
2G	3.6	0.8	18	192	na	0.03	0.13	0.7	90	na
2H	5.0	0.6	15	75	na	0.05	0.13	1.0	53	na
air freshener (AFR-1)										
2I	5.0	0.4	10	51	51	0.04	0.08	0.7	33	45
2J	2.3	0.9	20	90	90	0.02	0.05	0.3	37	65
2K	4.3	0.2	6	21	21	0.04	0.07	0.6	15	15

^a Mass concentration of particles assuming density of 1.0 g cm⁻³; na: data not available

Table 4.7. Summary of experiments involving simulated use of cleaning products (GPD-1 and GPC-1) and an air freshener (AFR-1), investigating the influence of ozone.

Expt	Product ^a	Amt ^b	O ₃ ^c	Start date (2005)	Start time	AER (h ⁻¹) ^d	T (°C) ^e	RH (%) ^f
3A	GPD-1	6.7 g		5-Jun	11:10	0.99	22.2	36
3B	GPD-1	3.7 g		9-Jun	10:00	1.03	23.2	56
3C	GPD-1	3.7 g	✓	12-Jun	10:30	1.04	22.4	45
3D	GPC-1	52 g		3-Jun	11:00	1.08	22.7	46
3E	GPC-1	52 g		21-Jun	9:30	1.01	23.2	48
3F	GPC-1	51 g	✓	7-Jun	9:40	1.16	23.9	36
3G	GPC-1	50 g	✓	14-Jun	9:10	0.99	22.2	48
3H	GPC-1	50 g	✓	23-Jun	10:00	1.00	21.8	53
3I	H ₂ O/Mop	-	✓	2-Jun	10:32	1.03	22.8	44
3J	AFR-1	45 mg/h		26-Jun	7:10	0.99	20.8	53
3J	AFR-1	43 mg/h	✓	26-Jun	12:10	1.00	21.3	54
3K	AFR-1	31 mg/h		27-Jun	12:00	1.01	21.1	53
3K	AFR-1	29 mg/h	✓	27-Jun	17:00	0.95	21.4	55

^a GPD-1 sprayed onto 0.11 m² sheet aluminum, surface wiped dry with paper towels after 1 min, towel and product removed (~2 min procedure). GPC-1 applied in dilute solution to 3.9 m² of vinyl flooring using sponge mop (~7 min procedure). AFR-1: set to “low” and plugged into electrical outlet for 2 days before experiment 3J; setting switched to “high” for experiment 3K.

^b Amount of product dispensed. For GPD-1 and AFR-1, the vast majority of dispensed product was released to chamber air. For GPC-1, much of the dispensed product remained in solution and was removed from the chamber when mopping was completed.

^c “✓” indicates that ozone was added to supply air at a level of 114-120 ppb; otherwise, no ozone in supply or chamber air.

^d Air exchange rate determined from measured decay of injected SF₆. Uncertainty estimated at ± 0.02-0.05 h⁻¹ based on standard deviation of *n* = 3 determinations in each of experiments 3C, 3E, and 3H.

^e Mean temperature over 12 h for experiments 3A-3I; mean over 5 h for each phase of experiments 3J-3K. Standard deviations were ≤ 0.3 °C except for experiments 3B (1.0 °C), 3E (1.1 °C) and 3F (1.4 °C). For additional details, see Appendix E, Figures E.23-E.25.

^f Mean RH over same periods shown for temperature. Standard deviations were ≤ 3% RH for all but experiment 3B (5%). For additional details, see Appendix E, Figures E.26-E.28.

Table 4.8. Time-averaged concentrations (ppb) of GPC-1 constituents during experiments 3D-3H.

		No ozone (Expts. 3D-3E) ^a				With ozone (Exps. 3F-3H) ^b	
Analyte ^c	CAS #	0-0.5 h	0.5-1.5 h	1.5-4 h	4-12 h	0-0.5 h	0.5-1.5 h
Terpene HCs							
α-Pinene	80-56-8	12.5	7.1	2.2	0.2	12.2	6.0
Camphene	79-92-5	12.1	6.3	1.8	0.2	12.2	6.0
α-Phellandrene ^d	99-83-2	9.3	4.6	1.1	0.2	8.7	2.6
α-Terpinene	99-86-5	19.9	8.8	1.3	0.2	3.9	nd
d-Limonene	5989-27-5	166	82	23	4.8	159	66
γ-Terpinene	99-85-4	18.0	8.9	2.5	0.5	17.5	6.7
Terpinolene	586-62-9	129	61	11.8	2.9	134	33
Terpene Alcohols							
1-Terpineol ^d	586-82-3	33	14.5	6.0	1.8	33	14.7
β-Terpineol ^d	138-87-4	10.6	5.2	2.3	0.9	10.5	5.1
4-Terpineol ^d	562-74-3	7.8	3.7	1.7	0.6	8.7	3.5
α-Terpineol	98-55-5	103	55	26	10.7	105	53
γ-Terpineol	586-81-2	14.1	6.5	2.5	0.9	13.3	4.4
Other VOCs							
p-Cymene	99-87-6	15.1	7.3	2.2	0.6	14.7	7.3
Eucalyptol	470-82-6	39	17.5	3.5	0.5	39	17.3

^a Mean of 2 experiments without ozone.

^b Mean of 3 experiments with ozone. For the most ozone-reactive compounds (α -terpinene, terpinolene, d-limonene, α -terpineol, γ -terpineol), concentrations reported for the 30-90 min “with O₃” category may be biased low owing to degradation of these compounds on Tenax samplers exposed to ozone.

^c Compounds listed by retention time (RT) within group.

^d Quantified by total ion current based on d-limonene response. α -Phellandrene identity confirmed with pure standard. Terpineols tentatively identified by matching mass spectra to NIST database. Uncertainty in TIC quantitation estimated as $\pm 30\%$ or less. Also tentatively identified were terpene HCs eluting at 26.3, 28.2, and 29.4 min; 0-30 min concentrations of these compounds were estimated by TIC to be 4-8 ppb.

Table 4.9. Chamber air concentrations and percent reacted of AFR-1 constituent terpenoids and other VOCs based on concentrations measured 0-5 h before and 3-5 h after ozone was introduced into the supply air at 114 ppb (Expt 3J). ^a

Analyte	CAS #	Steady VOC concentration without O ₃ (ppb) ^a	Homogeneous consumption of VOC by O ₃ (h ⁻¹) ^b	Steady VOC concentration with O ₃ (ppb) ^c	Homogeneous consumption of O ₃ by VOC (h ⁻¹) ^d
<i>Ozone-reactive VOCs</i>					
d-Limonene	5989-27-5	2.7 ± 0.3	0.88	1.43	0.03
Dihydromyrcenol	18479-58-8	11.2 ± 1.2	0.005	10.7	0.00
Linalool	78-70-6	7.3 ± 0.9	1.85	2.6	0.10
Linalyl acetate ^e	115-95-7	3.6 ± 0.3	1.75	1.32	0.05
β-Citronellol	7540-51-4	1.78 ± 0.18	0.99	0.89	0.02
α-Citral	141-27-5	0.45 ± 0.05	(f)	(f)	(f)
<i>Other VOCs</i>					
Benzyl acetate	140-11-4	16.7 ± 1.6	-	15.5 ± 0.2	-
Bornyl acetate	76-49-3	4.6 ± 0.5	-	4.3 ± 0.1	-

^a VOC concentrations in chamber air (mean ± 1 std. dev.) based on n = 4 measurements over period 0-5 h before ozone was introduced into the supply air at 114 ppb. Volatilization rate of air freshener constituents measured by mass difference to average 45.2 mg/h for the “without ozone” period and 43.3 mg/h for the “with ozone” period, a difference of 4%.

^b Consumption of VOC by homogeneous gas-phase reaction under steady-state conditions; calculated using published bimolecular reaction rates (see text) and steady O₃ concentration measured 3-5 h after O₃ introduced to chamber.

^c Steady-state concentrations with O₃ calculated for ozone-reactive VOCs and measured for other VOCs. Calculation based on VOC emission from air freshener, removal by ventilation and loss by homogeneous reaction. Emission rates were calculated from steady chamber air concentrations before ozone added, and thus include sorption effects. Measurements based on n = 3 samples collected 3-5 h after ozone was introduced.

^d Consumption of O₃ calculated using expected VOC concentrations and published bimolecular reaction rates.

^e Quantified by total ion current based on linalool response; identity confirmed by pure standard. Uncertainty in TIC quantitation estimated as ±30% or less.

^f Value could not be calculated because bimolecular reaction rate is not available.

Table 4.10. Measured TMB/PCE ratios and calculated OH concentrations for selected experiments.

Product	Expt(s)	Time (h) ^a	<i>n</i>	[TMB]/[PCE] ^b	[OH] ^c (10 ⁵ molec cm ⁻³)
GPD-1	3C	<i>t</i> < 0	4	1.735 ± 0.019	
		0 – 2	6	1.703 ± 0.008	1.0 ± 0.6
		2 – 12	9	1.610 ± 0.012	3.9 ± 0.7
		6 – 10	5	1.590 ± 0.016	4.6 ± 0.8

Product	Expt(s)	Time (h) ^a	<i>n</i>	[TMB]/[PCE] ^b	[OH] ^c (10 ⁵ molec cm ⁻³)
GPC-1	3G-3H	<i>t</i> < 0	4	1.695 ± 0.014	
		1 – 6	12	1.569 ± 0.005	3.9 ± 0.5
		8 – 10	4	1.598 ± 0.003	2.9 ± 0.4
		~ 12	3	1.653 ± 0.016	1.2 ± 0.6

Product	Expt(s)	Time (h) ^a	<i>n</i>	[TMB]/[PCE] ^b	[OH] ^c (10 ⁵ molec cm ⁻³)
AFR-1	3J-3K	<i>t</i> < 0	15	1.736 ± 0.003	
		1 – 5	12	1.661 ± 0.006	2.2 ± 0.2

^a Hours since start of experiment. For GPD-1 and GPC-1, experiment started (*t* = 0) with use of product in chamber already containing ozone; for AFR-1, experiment started with introduction of ozone into chamber already containing AFR constituents. Time intervals for analysis based on availability of data and trends observed in time-resolved measurements.

^b Molar ratio (ppb/ppb). Mean ± standard error. TMB concentrations were ~ 0.7 ppb.

^c Mean ± standard error. Calculated from [TMB]/[PCE] ratios.

Table 4.11. Measured concentrations (ppb) of very volatile carbonyls. ^a

Expt.	Product	Ozone	<i>n</i> ^b	Time (h) ^c	Formaldehyde	Acetaldehyde	Acetone
3A-3B	GPD-1		6	0-12	8.2 ± 2.2	1.0 ± 0.2	1.7 ± 0.7
3C	GPD-1	✓	2	0-4	23.7 (1.3)	2.2 (0.4)	3.9 (0.4)
3C	GPD-1	✓	2	4-12	17.9 (0.2)	1.9 (0.1)	2.5 (0.1)
3D-3E	GPC-1		8	0-12	7.3 ± 1.0	1.3 ± 0.4	2.1 ± 0.5
3F-3H	GPC-1	✓	6	0-4	16.0 ± 1.3	1.7 ± 0.5	31 ± 1
3F-3H	GPC-1	✓	6	4-12	12.0 ± 2.8	1.9 ± 0.5	12.4 ± 9.8
3I	Mop w/H ₂ O		4	0-12	9.8 ± 0.6	2.9 ± 0.2	1.8 ± 0.4
3J-3K	AFR-1		4	(-3)-0	4.1 ± 0.1	-0.4 ± 0.3	-0.5 ± 0.6
3J-3K	AFR-1	✓	4	2-5	11.2 ± 1.2	0.7 ± 0.4	14.2 ± 4.1

^a Mean ± standard deviation for *n* > 2, mean (absolute deviation) for *n* = 2. Multiple experiments under the same condition averaged.

^b Number of samples.

^c Time is relative to introduction of product for GPD-1 and GPC-1, and relative to the introduction of ozone for AFR-1.

Table 4.12. Secondary fine particulate matter formed during use of consumer products in relation to the presence of ozone. ^a

Expt	Product	Ozone	Maximum		Mean
			number (cm ⁻³)	mass (PM _{1.1} , µg m ⁻³)	mass (PM _{1.1} , µg m ⁻³)
3A	GPD-1		240	2.1	1.0
3B	GPD-1		520	3.3	1.6
3C	GPD-1	✓	44000	280	89
3D	GPC-1		620	4.5	3.5
3E	GPC-1		540	2.9	2.4
3F	GPC-1	✓	38000	138	36
3G	GPC-1	✓	35000	131	31
3H	GPC-1	✓	36000	132	34
3I	H ₂ O, mop	✓	840	5.1	3.5
3J	AFR-1		290	1.8	1.4
3J	AFR-1	✓	1550	6.9	4.8
3K	AFR-1		230	1.6	1.2
3K	AFR-1	✓	750	4.0	3.0

^a For GPD-1 (Expts 3A-3C) and GPC-1 (Expts 3D-3H), particle levels determined for 12-h period, starting with use of product; for AFR-1 (Expts 3J, 3K), values without ozone calculated for 5-h period before ozone introduced, values with ozone (“✓”) calculated for 5-h period after the start of ozone.

Table 4.13. Summary of findings from reactive chemistry experiments.

Bench-scale experiments.

- **Experimental design.** The constituents of cleaning products or an air freshener were exposed to ozone. The experiments were conducted with steady flow through a 198-L, Teflon-lined reaction chamber. For most experiments, the volatile constituents of the cleaning product were continuously supplied to the chamber. Ozone supply was suddenly initiated and then maintained for hours. Air in the chamber was continuously monitored for the concentrations of ozone and secondary organic aerosol. Sampling was also conducted for primary constituents of the cleaning product and volatile secondary species formed by chemical reactions. (§4.2)
 - **Experimental scope.** Three products were studied: a pine-oil based general-purpose cleaner (GPC-1); a d-limonene based general-purpose degreaser (GPD-1); and a plug-in scented-oil air freshener (AFR-1). Eleven experiments were conducted in which the volatile species of a selected product were exposed to ozone, at a constant inlet level that varied from ~ 30 ppb to ~ 250 ppb. The ventilation rate of the chamber was fixed at either one per hour or three per hour. One experiment was conducted in which the volatile constituents of GPC-1 were exposed to ozone and nitrogen dioxide. Three additional experiments were conducted in which the nominally dry product residue on a surface was exposed to ozone. (Table 4.1)
 - **Results: Ozone consumption.** Ozone was substantially consumed in each experiment. For the 12 experiments involving volatile constituents of the cleaning products, the residual ozone level in the chamber air was less than 20% of what it would have been without reactive chemistry. In the median case, reactive ozone consumption exceeded 90%. (Tables 4.2-4.5)
 - **Results: Primary VOC constituents.** With the pine-oil based cleaner, α -terpinene reacted strongly and unambiguously in all experiments (67-96% consumed). Four other chemicals — d-limonene, terpinolene, α -terpineol, and γ -terpinene — reacted substantially in some, but not all test conditions. For the general-purpose degreaser, d-limonene was consumed at levels corresponding to 10-20% of the supply concentration. Several VOCs in the air freshener exhibited substantial reactivity, including d-limonene (22-29% consumed), linalool (20-41%), linalyl acetate (19-25%), and β -citronellol (25-40%). (Tables 4.2-4.5)
 - **Results: Volatile oxidation product formation.** Several stable volatile oxidation products were detected and quantified in at least some of the experiments: formaldehyde, acetaldehyde, acetone, glycolaldehyde, formic acid, and acetic acid. Formaldehyde is of particular interest as a toxic air contaminant with a relatively low reference exposure level. Formaldehyde yields, expressed as the moles of formaldehyde generated per mole of ozone consumed, were in the range 16-28% for the experiments involving the volatile constituents of the cleaning products. With the air freshener, formaldehyde yields were 29-90%. (Tables 4.2-4.5)
 - **Results: Hydroxyl radical.** OH concentrations were indirectly determined to be in the range $\sim 10^4$ to $\sim 10^7$ molecules per cm^3 . These are consistent in magnitude with the few similar prior investigations from the literature. A simplified model of OH formation and destruction captured the overall dependence on experimental conditions reasonably well. (Figure 4.3)
 - **Results: Secondary organic aerosol.** Nucleation events, in which new particle formation was observed when cleaning product constituents were first exposed to ozone, were observed in 14 of the 15 experiments. Strikingly, such events were even observed when only the nominally dry surface residue of cleaning products GPC-1 or GPD-1 were exposed in the chamber to ozone. (Figures 4.4-4.5 and D.1-D.23)
-

Table 4.13. (continued)

Room-scale experiments

- **Experimental design.** Simulated-use experiments were conducted with cleaning products and air fresheners in a room, with and without the deliberate addition of ozone to the room air. The chamber was continuously ventilated at one air exchange per hour. For experiments involving cleaning product use in the presence of ozone, the room conditions were first stabilized with a steady supply of ozone and then the simulated activity commenced. For experiments involving the air freshener in the presence of ozone, the room conditions were first stabilized with the air freshener in operation and then ozone was added. Room air was continuously monitored for the concentrations of ozone and secondary organic aerosol. Sampling was also conducted to measure the primary constituents of the cleaning product or air freshener, and the volatile secondary species formed by chemical reactions. (§4.4)
 - **Experimental scope.** Three products were studied. A pine-oil based general-purpose cleaner (GPC-1) was used in dilute solution in a floor-mopping application. A d-limonene based general-purpose degreaser (GPD-1) was used full-strength in a surface-cleaning application. A plug-in scented-oil air freshener (AFR-1) was operated as designed. Eleven experiments were conducted, of which seven involved ozone supply. (Table 4.7)
 - **Results: Ozone consumption.** Ozone was substantially consumed in the experiments that involved cleaning-product use. Shortly after cleaning product use, the ozone level would decline from its stable level in room air of ~ 60 ppb to ~ 5 ppb. The ozone level would then slowly recover over then next 12 h, approaching its initial undisturbed value. The air freshener had a noticeable effect on the ozone levels, although much smaller than did the cleaning products. (Figure 4.9)
 - **Results: Primary VOC constituents.** The presence of ozone did not significantly influence the short-term peak concentrations of primary constituents associated with cleaning product use. However, the time-series concentrations of several constituents were observed to decline more rapidly with ozone than without. Noteworthy in this regard were d-limonene, terpinolene, and α -terpineol. For the air freshener, the introduction of ozone led to substantial decreases in the room-air concentrations of d-limonene, linalool, linalyl acetate, and β -citronellol. (Figures 4.6-4.8)
 - **Results: Volatile oxidation product formation.** The most noteworthy stable volatile byproduct measured was formaldehyde. For the simulated cleaning activities, the 12-h average formaldehyde level was 7-8 ppb for the experiments without ozone and 20 ppb (GPD-1) or 13 ppb (GPC-1) for the experiments with ozone. The addition of ozone to room air with air freshener use increased the formaldehyde level from 5 to 11 ppb. (Table 4.11)
 - **Results: Hydroxyl radical.** Indirectly measured OH concentrations were $(1-5) \times 10^5$ molecules cm^{-3} . (Table 4.10)
 - **Results: Secondary organic aerosol (SOA).** The combined presence of cleaning product or air freshener constituents with ozone led to measured changes in fine particle levels that were slight (AFR-1), moderate (GPC-1) or strong (GPD-1). In particular, the 12-h average concentration of fine particulate matter with the use of GPD-1 was $1-2 \mu\text{g m}^{-3}$ without ozone, yet $89 \mu\text{g m}^{-3}$ with ozone. (Table 4.12)
-

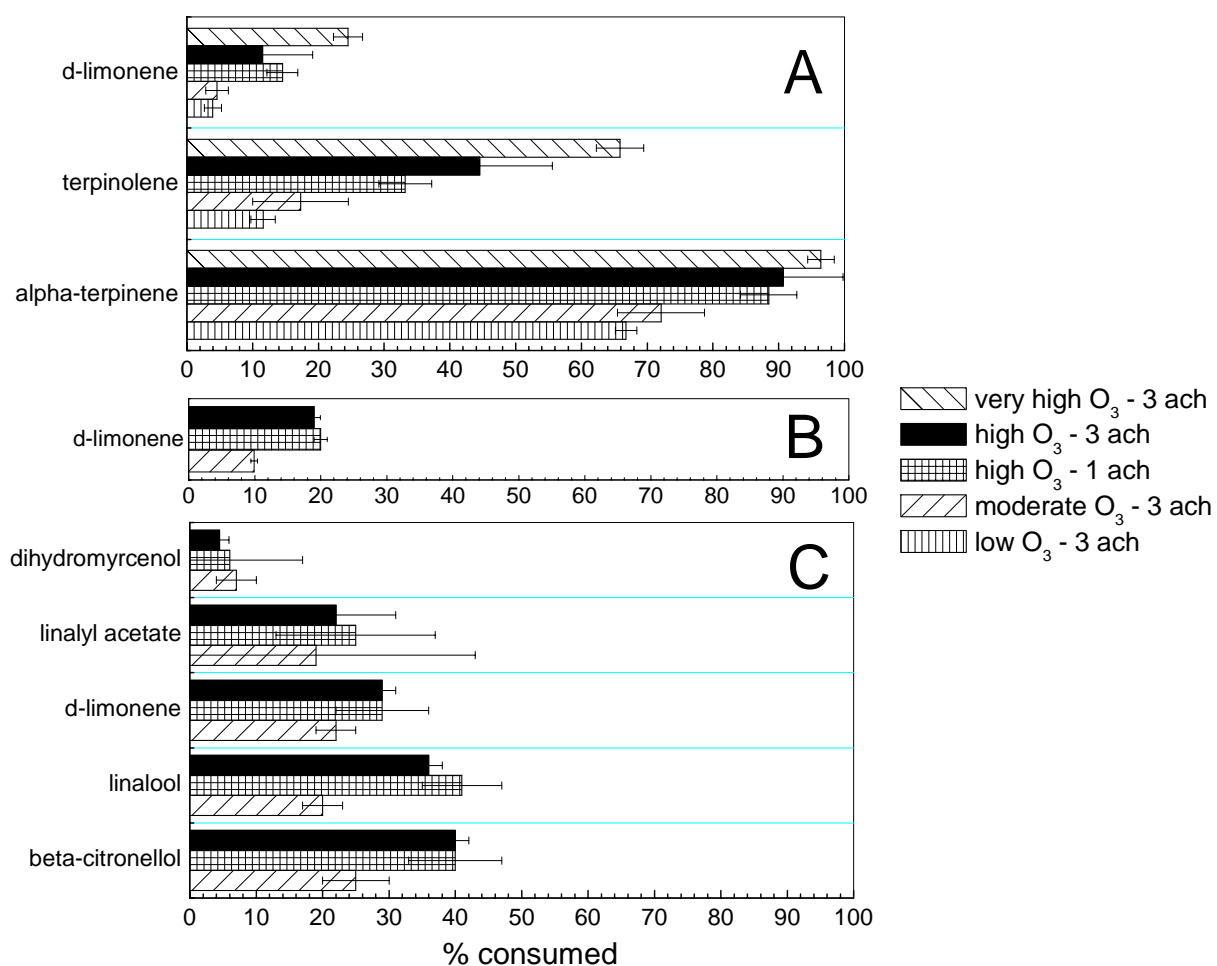


Figure 4.1. Consumption of reactive VOCs from (A) GPC-1, (B) GPD-1, and (C) AFR-1.

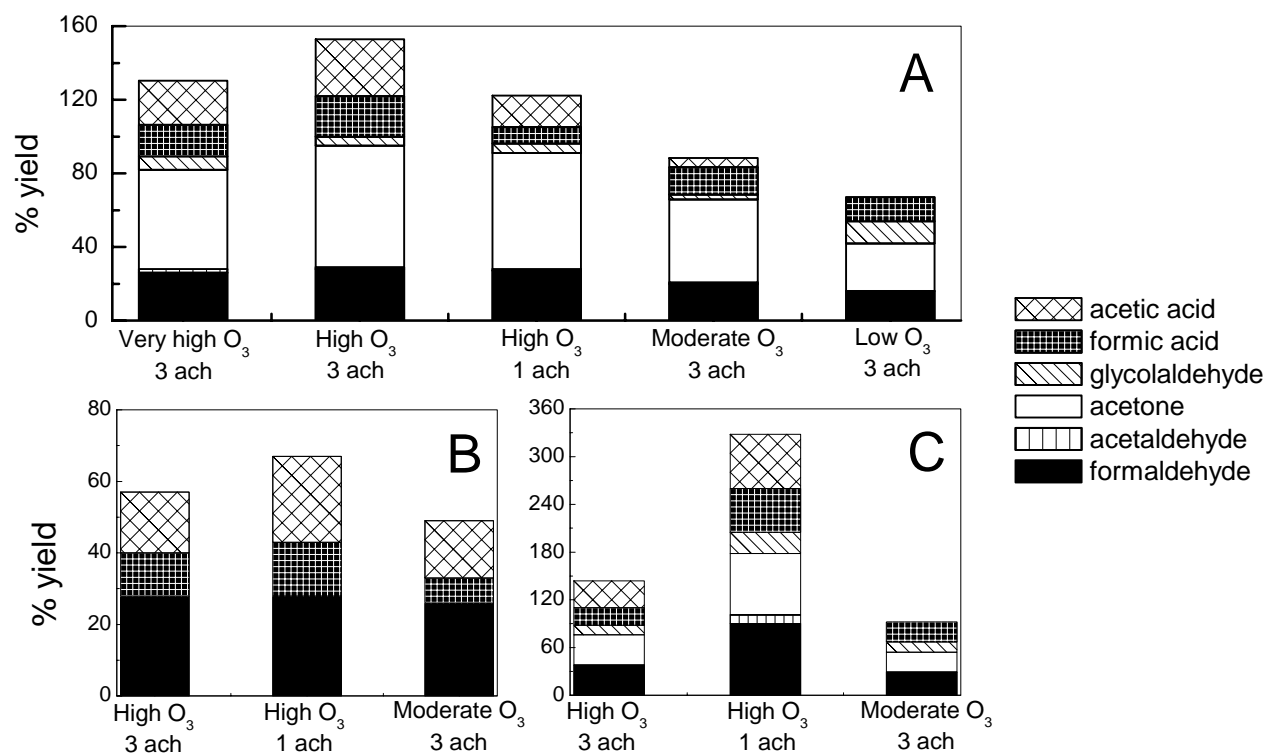


Figure 4.2. Yield of oxidation products from ozone reaction with volatile components of (A) GPC-1, (B) GPD-1, and (C) AFR-1.

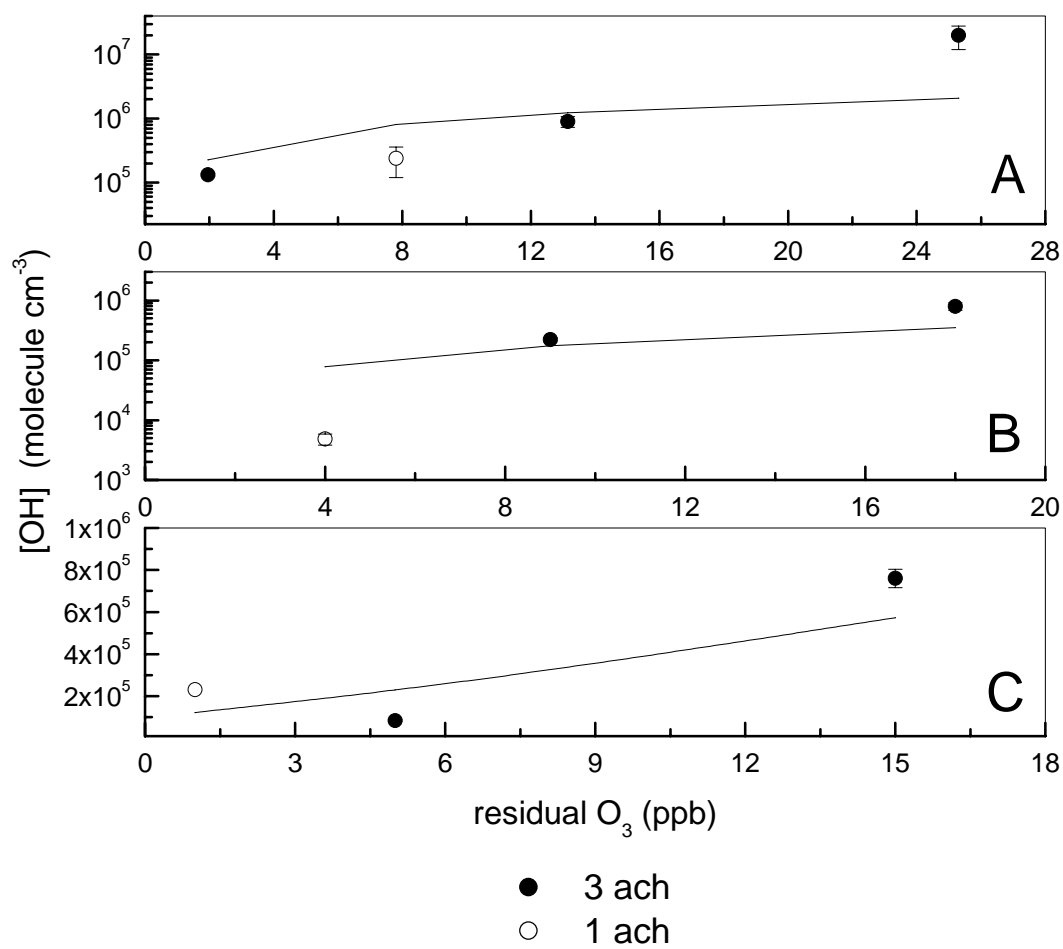


Figure 4.3. Hydroxyl radical concentration versus residual ozone concentration for small-chamber experiments with (A) GPC-1, (B) GPD-1, and (C) AFR-1.

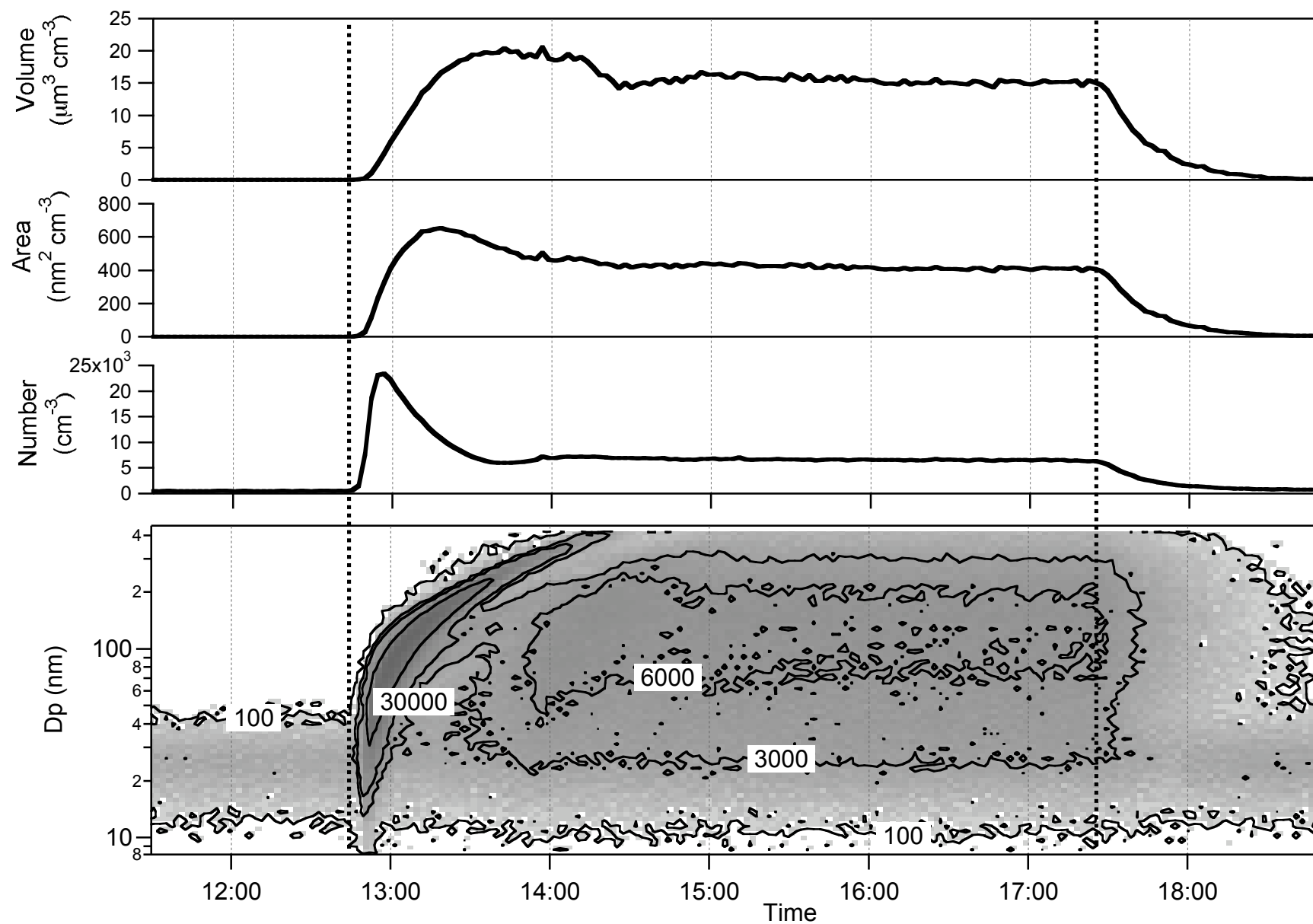


Figure 4.4. SMPS measurements of secondary organic aerosol particles generated in the reaction of AFR-1 with moderate ozone levels (63 ppb in supply air) at 3 ach (Expt 2K).

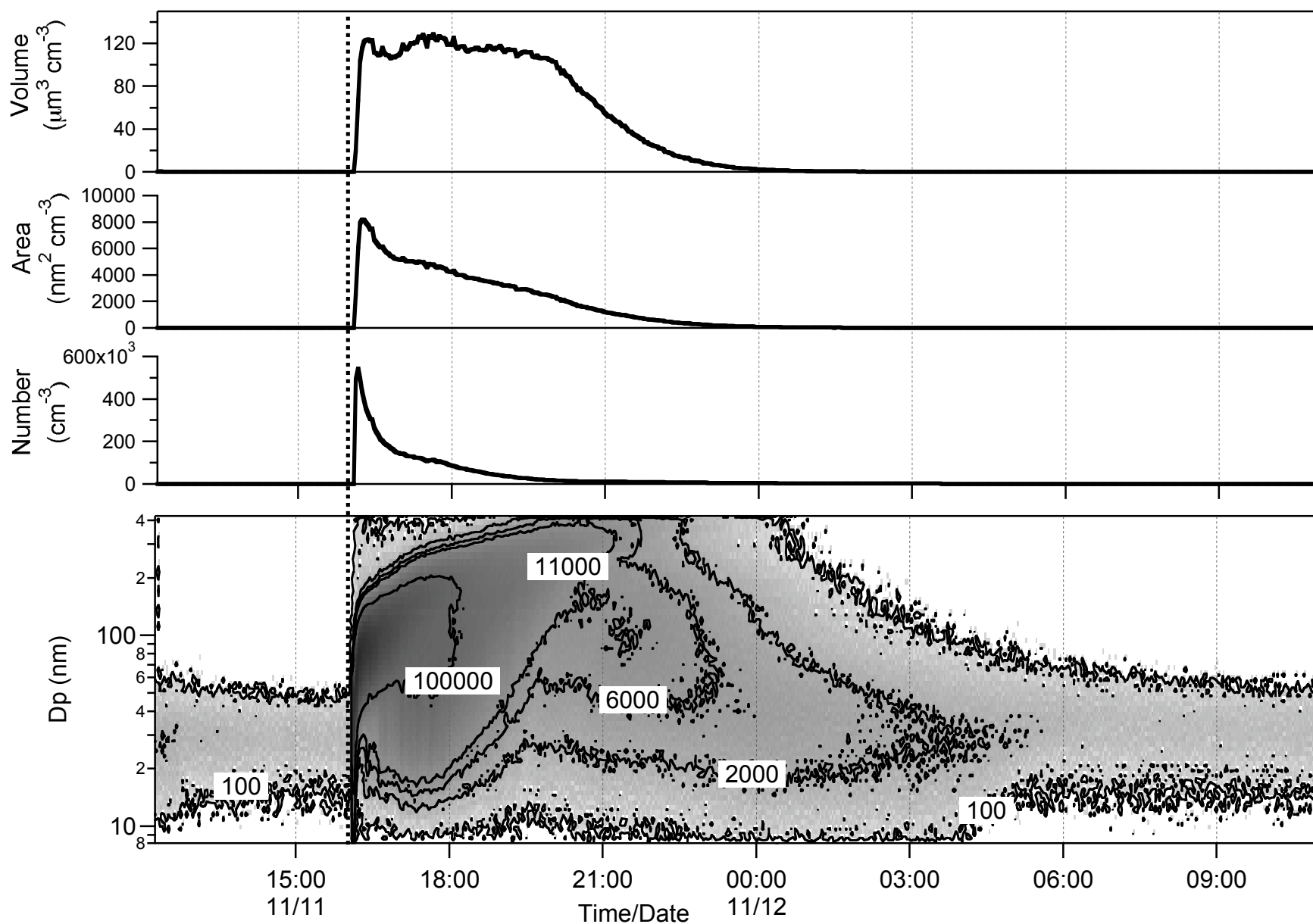


Figure 4.5. SMPS measurements of secondary organic aerosol particles generated in the reaction of dried residue of GPC-1 with high ozone levels (118 ppb in supply air) at 1 ach (Expt 2L).

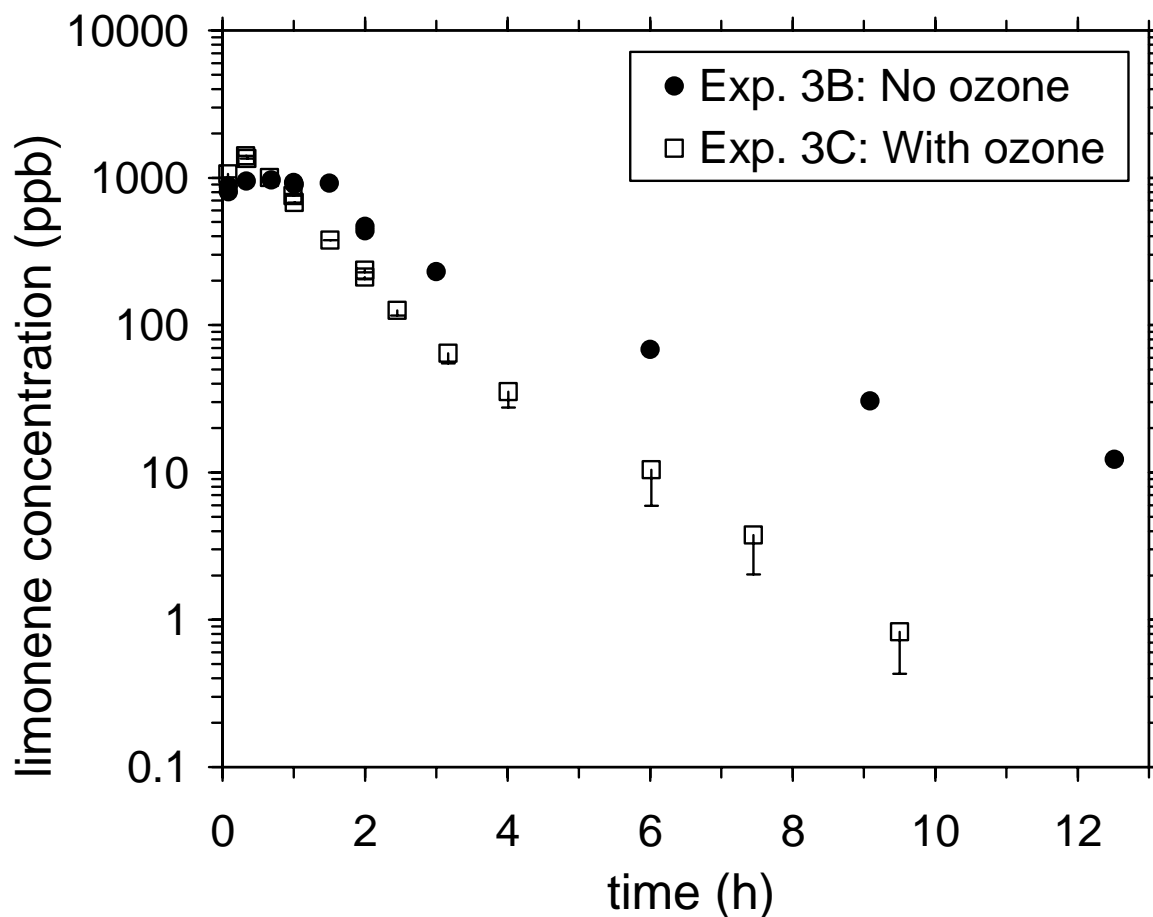


Figure 4.6. Limonene concentrations in chamber air following application of the orange oil degreaser (GPD-1). Data have been adjusted to account for ozone-induced degradation of limonene on Tenax; the symbol represents the corrected value and the T-bar extends down to the measured value. Adjustments based on Figures 1-2 of Calogirou et al. (1996).

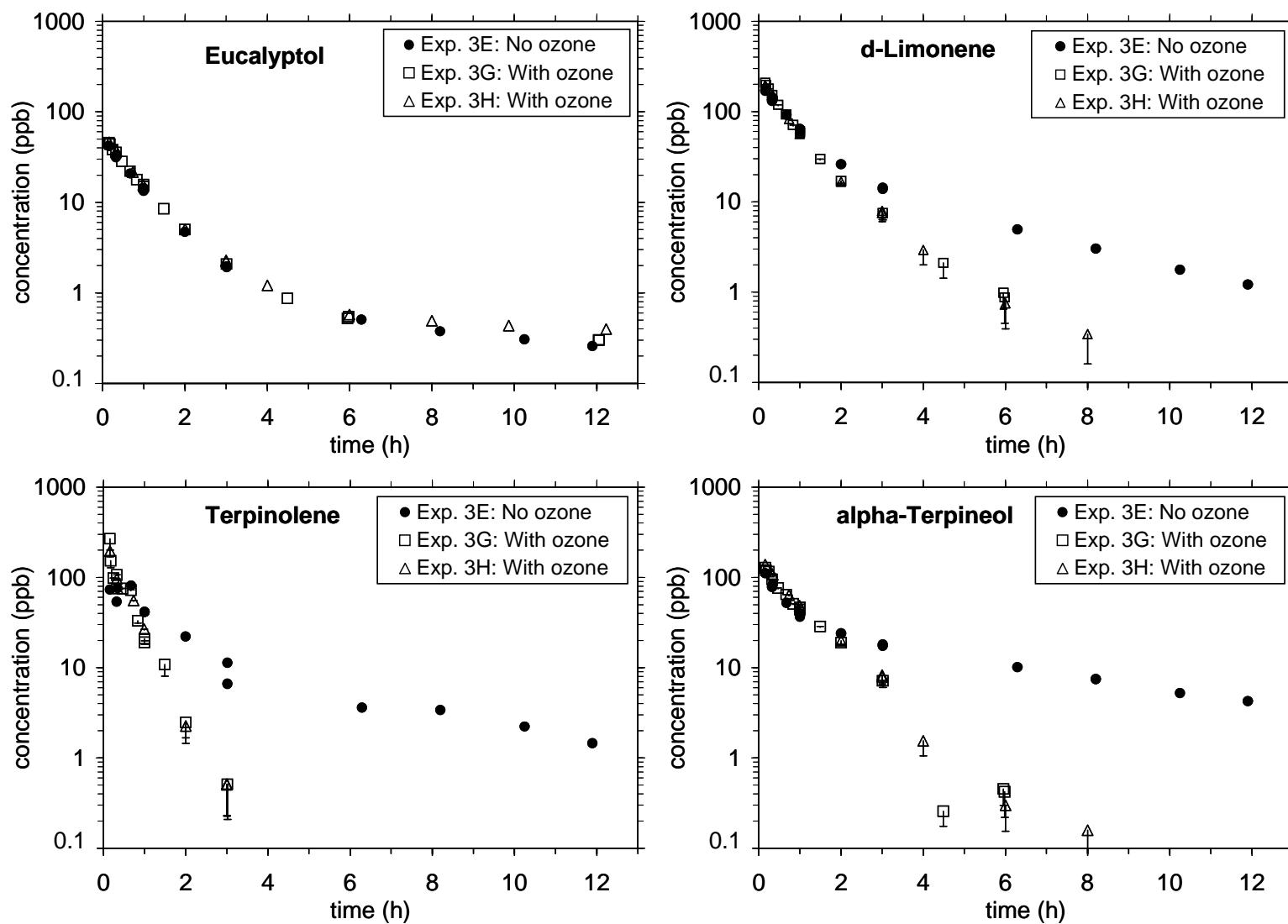


Figure 4.7. Constituent concentrations in chamber air following floor mopping with a dilute solution of the pine oil cleaner (GPC-1). Data for Exps. 3G-3H have been adjusted to account for ozone-induced degradation of limonene on Tenax; the symbol represents the corrected value and the T-bar extends down to the measured value. Adjustments based on Figures 1-2 of Calogirou et al. (1996).

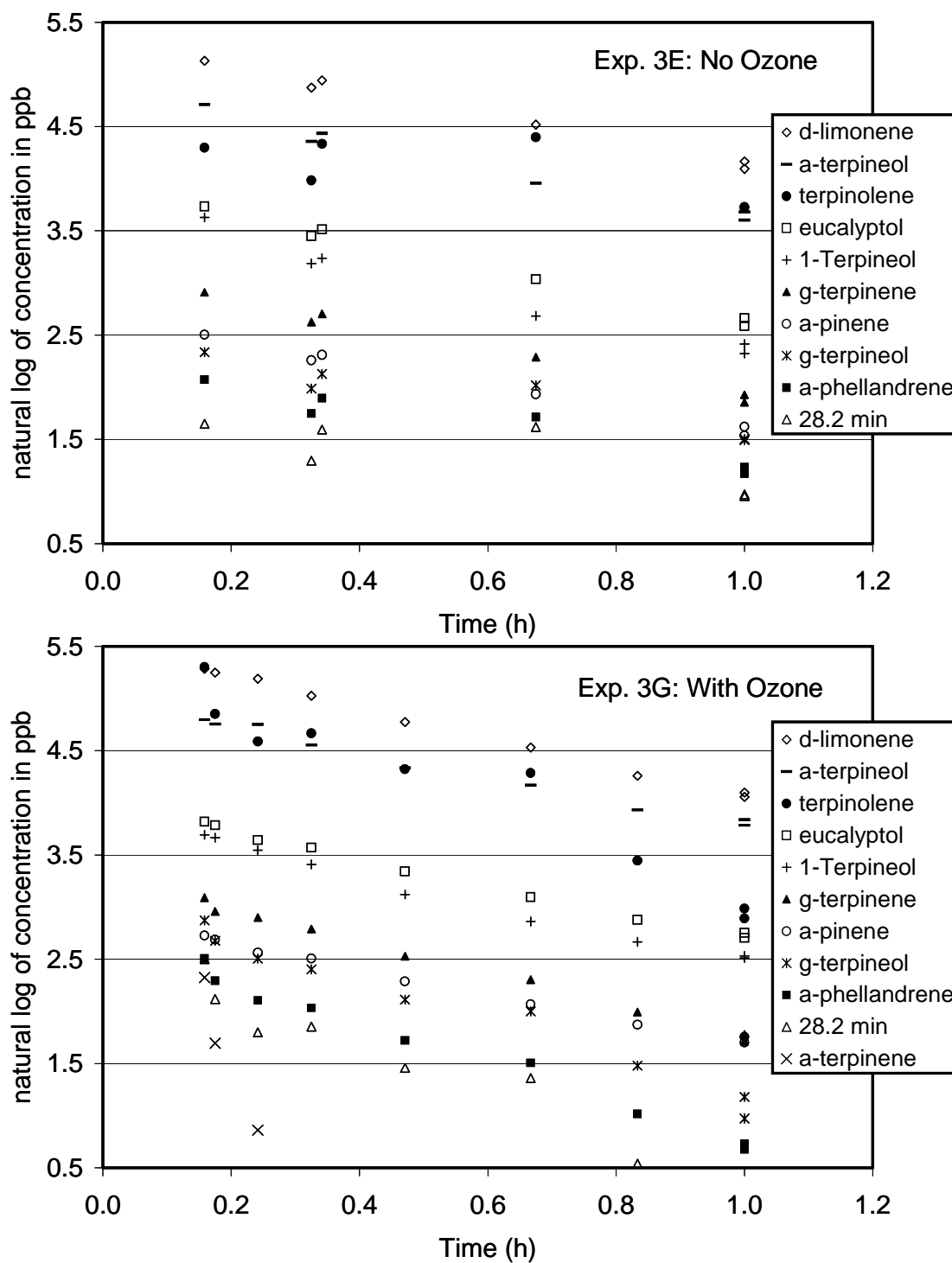


Figure 4.8. Constituent concentrations in chamber air for 1 hour following floor mopping with a dilute solution of the pine oil cleaner (GPC-1). Data presented as natural logarithm of concentration to elucidate the relative decay rates of various compounds with and without ozone present.

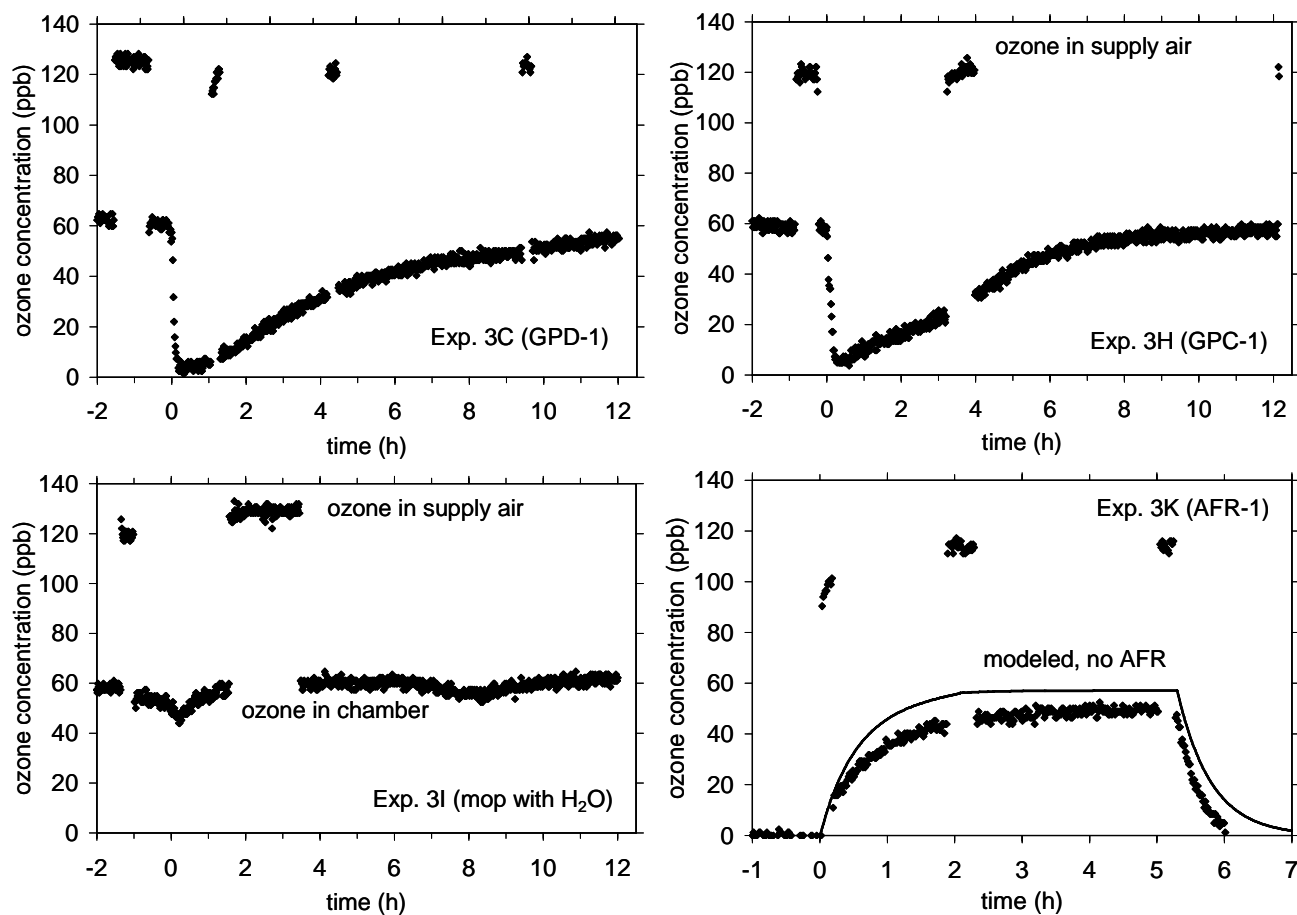


Figure 4.9. Ozone concentration profiles: (a) Exp. 3C: GPD-1 sprayed at t=0; (b) Exp. 3H: mopping with GPC-1 started at t=0; (c) Exp. 3I: mopping with water only; (d) Exp. 3K: AFR-1 plugged-in for >24 h then ozone added to chamber air supply starting at t=0.

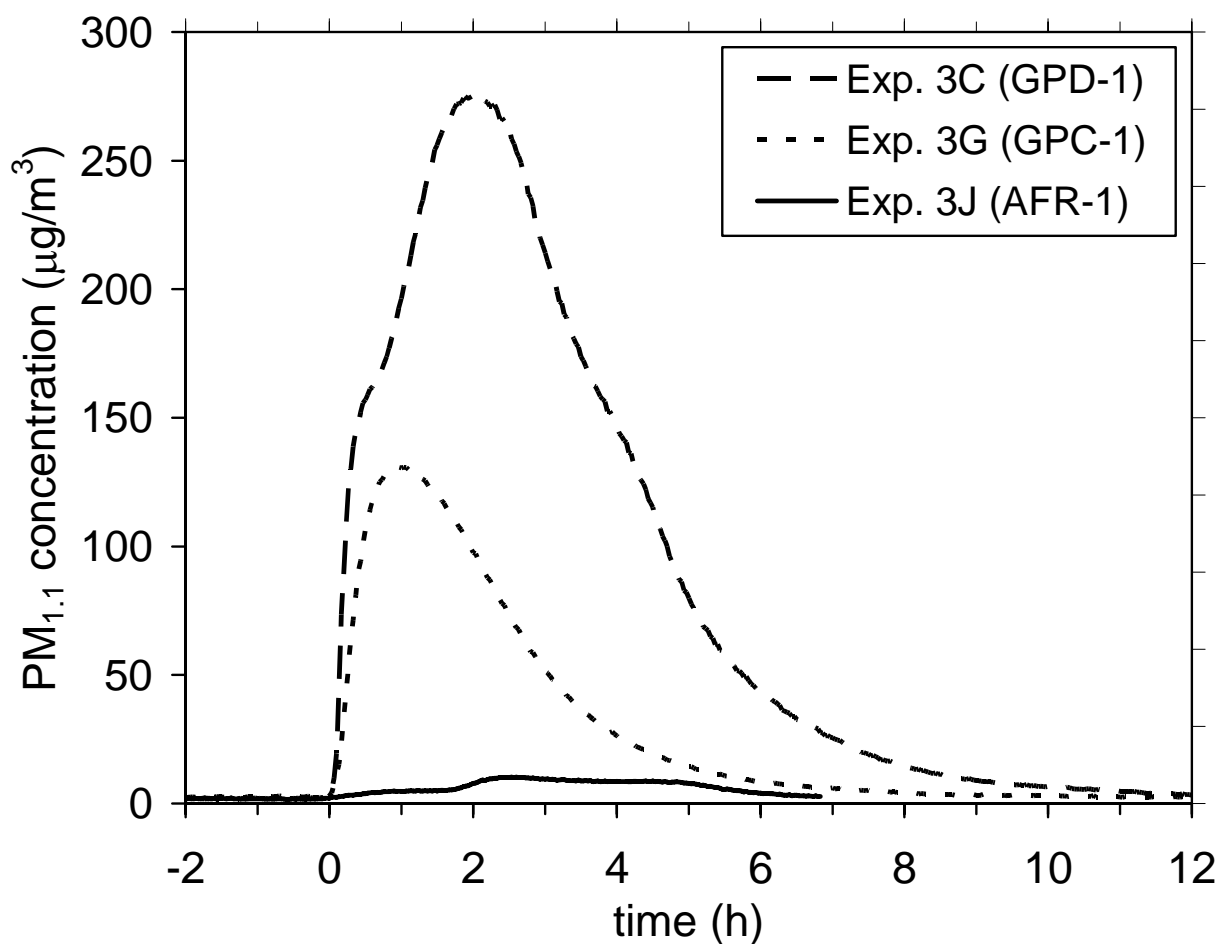


Figure 4.10. Particle mass concentrations calculated from the size-resolved particle number concentration data.

5. IMPLICATIONS FOR AIR-POLLUTANT EXPOSURE

Most individuals are exposed to both primary and secondary pollutants from cleaning products. With the present study, we have better defined these exposures for a subset of products under a variety of typical use scenarios. This section of the report explores the significance of the new research findings for informing our understanding in inhalation exposure to selected air pollutants owing to the use of cleaning products and air fresheners in residences. The emphasis in this exploration is on 2-butoxyethanol as a primary constituent and on formaldehyde and secondary organic aerosol as secondary species. The section begins with the analysis of a series of exposure scenarios. Then some limitations of our understanding of exposure resulting from cleaning product use are discussed, emphasizing the uncertainty in reactive chemistry and toxicology. Finally, some suggestions are offered for how exposures might practically be reduced, even while continuing to use the same products.

5.1. Illustrative exposure scenarios

5.1.1. Example 1: Routine cleaning by occupant

For many use-patterns, the resulting concentrations of the constituents and their reaction products fall within ranges that lead to what are currently considered to be modest exposures and subsequent intakes. As an example, consider the intake of 2-butoxyethanol (2-BE), formaldehyde and secondary organic aerosol (SOA) for an occupant of a home or large apartment who does her or his own cleaning. In this example the inhalation intakes from different cleaning activities over a one-year period are first calculated, and then the intakes are reported as daily averages. Table 5.1 shows the assumed cleaning activities, their frequency of occurrence and duration, as well as the duration of the exposure. The activity patterns in the table are based, in large part, on values from Table 15-12 of the US EPA Exposure Factor Handbook (1997). The breathing rates are taken from Table 5-6 of this same source; these values, in turn, are based largely on the work of Adams (1993). The air-exchange rate is assumed to average 1 h^{-1} .

The exposure to 2-butoxyethanol results from direct exposure to 2-BE from cleaning products GPC-2, GPC-3 and GLC-1. The exposures to formaldehyde and SOA are a consequence of ozone-initiated chemistry with the reactive constituents of GPC-1, GPD-1 and AFR-1. In evaluating the reactive chemistry, we have assumed that the home or apartment is not air-conditioned and that the indoor ozone level is 15 ppb during cleaning activities and averages 10 ppb over a daily cycle (Lee et al., 1999; Weschler, 2000). As constructed, this scenario represents a high-end exposure among the set of occupants who clean their own dwellings. We say this because the cleaning schedule is aggressive (although it is taken from the USEPA Exposure Factor Handbook), because the occupant is assumed to spend a large fraction of each day in the dwelling that is being cleaned, and because the indoor ozone concentrations are at the high end of daily averages.

The analysis summarized in Table 5.1 includes both exposures that occur during the cleaning event (duration listed in the 4th column of Table 5.1) and those that occur after the event (duration obtained from the difference between the 5th and 4th columns of Table 5.1). The latter accounts for the fact that people frequently remain in the area after the cleaning activity has been completed. The total exposure duration (i.e., the sum of the time required for the activity plus the time remaining in the location after the activity) is based on the location of the cleaning event and varies from 0.42 h for mopping the bathroom floor to 12 h for interior window cleaning. It is assumed that the occupant is breathing at a higher rate ($1.33 \text{ m}^3 \text{ h}^{-1}$) during the activity than after the activity ($0.48 \text{ m}^3 \text{ h}^{-1}$). In the case of the air freshener, it is assumed that the occupant is in the

home or apartment 18 h/day, is active for two of these hours (breathing rate of $1.33 \text{ m}^3 \text{ h}^{-1}$) and is sedentary (sitting or sleeping) for the remaining 16 h/day (breathing rate of $0.48 \text{ m}^3 \text{ h}^{-1}$).

The annual inhalation intake (mg/y) has been calculated as the sum of the annual intake during the activity and the annual intake during post-activity periods. More specifically, the annual intake during the activity was calculated as the product of the number of days in a year that the activity occurred (d/y), the hours per day required to perform the activity (h/d), the average concentration during the activity (mg m^{-3}) and the breathing rate during the activity ($1.33 \text{ m}^3 \text{ h}^{-1}$). The annual intake post-activity was calculated as the product of the number of days in a year that the activity occurred, the hours per day of post-activity exposure, the average concentration during the post-activity exposure, and the breathing rate during the post-activity exposure ($0.48 \text{ m}^3 \text{ h}^{-1}$).

Based on the stated assumptions, the experimental results presented in §3 and §4 of this report, and the outlined method for executing the calculations, the final three columns of Table 5.1 show the estimated annual intakes of 2-BE, formaldehyde, and SOA attributable to each of the listed activities involving household cleaning products and air fresheners. By summing the intakes from each of the activities, we estimate that the hypothetical home or apartment dweller has a total average daily intake of $3000 \mu\text{g d}^{-1}$ (or 3 mg d^{-1}) for 2-BE, $21 \mu\text{g d}^{-1}$ for HCHO and $35 \mu\text{g d}^{-1}$ for SOA. The 2-BE value of $3000 \mu\text{g d}^{-1}$ can be compared with the estimate of Zhu et al. (2002) of 5300 and $13,200 \mu\text{g d}^{-1}$ for a homeowner using two all-purpose spray cleaners, and 280 and $450 \mu\text{g d}^{-1}$ for two spray glass-cleaners.

In this and the following examples, it is difficult to evaluate the health implications of the calculated annual inhalation intakes (except for formaldehyde), because health-based regulatory standards are not directly applicable to such intakes. That said, we can make rough comparisons with existing standards to put these results into perspective. In the case of 2-BE, California has established an acute one-hour exposure limit of 14 mg m^{-3} (OEHHA, 1999). For a breathing rate of $1.3 \text{ m}^3 \text{ h}^{-1}$, this results in an intake of 18 mg during the one hour of acute exposure. The federal reference concentration for chronic inhalation exposure (RfC) is 13 mg m^{-3} (<http://www.epa.gov/iris/subst/0500.htm>). Assuming that the typical adult inhales between 12 and 15 m^3 of air per day (USEPA, 1997), exposure at the RfC corresponds to a daily intake of 156 to 195 mg. Compared with these intakes, the average 2-BE intake of 3 mg d^{-1} calculated in the present scenario is relatively modest.

The daily formaldehyde intake of $21 \mu\text{g d}^{-1}$ is below California's "no significant risk level" (NSRL) of $40 \mu\text{g d}^{-1}$. (NSRLs have not been established for 2-BE and SOA.)

We know of no existing health standards or guidelines that specifically address exposure to SOA. There are standards that apply to the ambient aerosol (PM_{10} and $\text{PM}_{2.5}$ National Ambient Air Quality Standards and California Air Resources Board standards), and SOA is present as an important component of ambient aerosols. However, ambient SOA is only one of many components of the ambient aerosol and its particular role in contributing to adverse health outcomes is unknown. Also, while similar, its chemical composition is not identical to the SOA formed from ozone-terpene chemistry that is relevant for indoor use of cleaning products and air fresheners. For the purpose of preliminary exploration, let us assume that the toxicological properties of SOA and $\text{PM}_{2.5}$ were equivalent. The 24-h national ambient air quality standard (NAAQS) for $\text{PM}_{2.5}$ is $65 \mu\text{g m}^{-3}$. California does not have a 24-h standard for $\text{PM}_{2.5}$ but has established a 24-h standard of $50 \mu\text{g m}^{-3}$ for PM_{10} . (The NAAQS and California state standards for annual average concentrations of $\text{PM}_{2.5}$ are 15 and $12 \mu\text{g m}^{-3}$, respectively.) Given that the typical adult inhales between 12 and 15 m^3 of air per day, the 24-h NAAQS of $65 \mu\text{g m}^{-3}$ is

equivalent to a daily inhalation intake of 780-975 μg of $\text{PM}_{2.5}$. The daily SOA intake of 35 μg calculated in the present example is much smaller than this level.

A second comparison can be made using results from epidemiology studies. Numerous studies have shown associations between airborne particle levels, as measured at ambient monitoring stations, and short-term morbidity and mortality. For example, Pope et al. (2002) report that each 10 $\mu\text{g m}^{-3}$ increase in fine particle concentration is associated with a 4% increased risk from all-cause mortality, a 6% increase in cardiopulmonary mortality, and an 8% increase in lung-cancer mortality. An average adult intake of 35 $\mu\text{g d}^{-1}$ for SOA is approximately equivalent to an increment of 2.5 $\mu\text{g m}^{-3}$ in daily average exposure concentration. If similar associations applied to the SOA generated by the reactions of ozone with cleaning product constituents as have been found by Pope et al. for ambient $\text{PM}_{2.5}$, then the additional daily SOA exposure concentration of 2.5 $\mu\text{g m}^{-3}$ calculated in the present example would be associated with approximately a 1% increased risk from all-cause mortality, a 1.5% increase in cardiopulmonary mortality, and a 2% increase in lung-cancer mortality.

However, evidence is largely lacking either to support or to refute the assumption that the toxicological properties of SOA and $\text{PM}_{2.5}$ are equivalent or even similar. The chemical composition of particles at ambient monitoring sites is expected to differ in meaningful ways from the secondary organic aerosol produced by ozone reactions with terpene hydrocarbons and terpene alcohols. On the other hand, secondary organic aerosol is an important contributor to ambient fine particulate matter levels. Also, there is no strong evidence that the adverse health effects associated with ambient PM are strongly tied to specific components. Additional studies are needed to evaluate the potential adverse health effects of SOA produced by processes similar to those described in this report.

5.1.2. Example 2: Multi-house cleaning by professional home cleaner

People who clean private homes for a living have a much larger exposure to cleaning agent constituents and their reaction products than calculated in the previous example. Table 5.2 is analogous to Table 5.1, but for the case of a professional home cleaner (i.e., a domestic cleaner). It shows the assumed cleaning activities, their frequency of occurrence, the hours per day spent at the activity on those days that the activity occurs and the duration of exposure (time spent on activity plus time in the area following the completion of the activity). It is assumed that the domestic cleaner works in four homes per day, five days per week for 50 weeks per year. In evaluating the impact of reactive chemistry, we have again assumed that the home is not air-conditioned and that the indoor ozone level is 15 ppb during cleaning activities (Lee et al., 1999; Weschler, 2000). It is further assumed that the domestic cleaner is moderately active throughout these activities and is breathing at a rate of 1.33 $\text{m}^3 \text{h}^{-1}$. In contrast to the previous example, air fresheners are not included in the assumed product mix that constitute the domestic cleaner's exposure.

Based on these assumptions and the experimental results presented in §3 and §4 of this report, we estimate that the hypothetical professional home cleaner in this example has a total average daily intake of 14 mg d^{-1} (14,000 $\mu\text{g d}^{-1}$) for 2-BE, 80 $\mu\text{g d}^{-1}$ for HCHO and 300 $\mu\text{g d}^{-1}$ for SOA. The 2-BE average daily intake of 14 mg , although almost five times higher than in the previous example, is still considerably smaller than a daily intake of 156-195 mg that would occur from exposure at the federal RfC for chronic inhalation exposure to 2-BE. The daily formaldehyde intake exceeds California's "no significant risk level" (NSRL) of 40 $\mu\text{g d}^{-1}$. The SOA average daily intake of 300 μg is approximately one-third the daily intake of $\text{PM}_{2.5}$ that

would occur from exposure at the 24-h average NAAQS level of $65 \mu\text{g m}^{-3}$, but is slightly larger than the inhalation intake that would occur from exposure at the annual average NAAQS level of $15 \mu\text{g m}^{-3}$.

Relative to these estimated exposures, it is worth noting that a cross sectional study of 4521 women by Medina-Ramón et al. (2003) found that asthma symptoms were significantly higher among women currently (OR 1.46, $n = 593$) or formerly (OR 2.09, $n = 1170$) employed in domestic cleaning. In total, 25% of the asthma cases in the study population were associated with employment as domestic cleaners.

5.1.3. Example 3: Cleaning in a small, moderately ventilated bathroom

Cleaning large surface areas in a small room over a short period can lead to high concentrations of cleaning product constituents, even at moderate ventilation rates.

The following example considers the use of GPC-2 to clean soap scum from a shower stall in a small bathroom (6.1 m^3). GPC-2 is recommended for such a task (Table 3.25). Assume that the bathroom is ventilated at 0.25 h^{-1} , and that it contains a shower stall with three $0.8 \times 1.8 \text{ m}$ ($2.7 \times 6 \text{ ft}$) panels and a shower curtain. Only the panels are cleaned; hence, the total area to be cleaned is 4.3 m^2 . By scaling the results reported for “Counter, full strength, spray and wipe only, towels retained” in Table 3.30, one obtains an estimate for the 1st hour gas-phase concentration for 2-BE of $177,000 \mu\text{g m}^{-3}$ (177 mg m^{-3} or 37,000 ppb). (The scaling requires two factors: one to account for the different loadings – $0.56 \text{ m}^2/50 \text{ m}^3$ vs. $4.3 \text{ m}^2/6.1 \text{ m}^3$ – and another to account for the different ventilation rates – 0.5 h^{-1} vs. 0.25 h^{-1} .) Note that $177,000 \mu\text{g m}^{-3}$, although high, is still roughly 20 times lower than 2-BE’s saturation vapor pressure at 25°C ($7.9 \times 10^{-4} \text{ atm} = 3.8 \times 10^6 \mu\text{g m}^{-3}$).

The bathroom concentration of $177,000 \mu\text{g m}^{-3}$ is more than an order of magnitude larger than California has established as the reference exposure level (REL) for acute (1 h) exposures to 2-BE ($14,000 \mu\text{g m}^{-3}$), as well as the federal reference concentration for chronic inhalation exposure, RfC ($13,000 \mu\text{g m}^{-3}$). Assuming that it takes 0.25 h to complete this task, the 2-BE exposure during this cleaning event is 9300 ppb-h. If the work is performed by an adult female at a breathing rate of $1.33 \text{ m}^3 \text{ h}^{-1}$, corresponding to a breathing rate anticipated during light exercise, her intake of 2-BE during this 15 minute cleaning event is approximately 60 mg. This is more than three times the one-hour intake of 18 mg derived from California’s acute one-hour exposure limit for 2-BE (see Example 1).

5.1.4. Example 4: Whole-house interior window cleaning

Another example of a cleaning activity that can result in relatively high exposures and intakes is interior window cleaning. Although products that are sold for this purpose caution that they should be used with adequate ventilation, there may be a tendency among some homeowners to keep the windows closed during this activity because it would make the overall task easier.

In this example assume a 130 m^2 (1400 ft^2) home with 2.4 m (8 ft) ceilings for a total volume of 320 m^3 (11200 ft^3) and that the windows have a total area of 25 m^2 . Further assume that “window-cleaning” is a whole house event and that the air-exchange rate is 0.2 h^{-1} during the cleaning activity, a low but plausible value (Murray and Burmaster, 1995). The exposures will be estimated based on information from Experiment 1L in Table 3.30. The product is dispensed by means of spraying 11 g of window cleaner GLC-1 per m^2 of cleaned surface. The total amount of cleaner dispensed is $(25 \text{ m}^2)(11 \text{ g m}^{-2}) = 275 \text{ g}$. The emission factor for 2-BE is

8.0 mg/g, while that for 2-hexyloxyethanol (2-HE, CAS 112-25-4) is 4.8 mg/g. Hence, a total of 2200 mg of 2-BE and 1320 mg of 2-HE are emitted into the household air during window cleaning. Assume that this occurs over a period of 2 hours, then the concentrations in the home (neglecting sorption) will be approximately 17 mg m^{-3} ($17,000 \text{ } \mu\text{g m}^{-3}$) for 2-BE and 10 mg m^{-3} ($10,000 \text{ } \mu\text{g m}^{-3}$) for 2-HE.

Assuming that it takes 2.0 h to complete this task, the 2-BE exposure during the window cleaning is 7000 ppb-h. If the work is performed by an adult female at a breathing rate of $1.33 \text{ m}^3 \text{ h}^{-1}$, corresponding to a breathing rate anticipated during light exercise, her intake of 2-BE during this two hour cleaning event is 45 mg. Analogously, her exposure to 2-HE is 3400 ppb-h and her intake is 27 mg during the actual window cleaning event.

The average 2-BE concentration of $17,000 \text{ } \mu\text{g m}^{-3}$ is larger than California's REL for acute exposures to 2-BE ($14,000 \text{ } \mu\text{g m}^{-3}$). The intake of 2-BE during the 2-hour event, 45 mg, is more than twice the one-hour intake of 18 mg derived from California's acute one-hour exposure limit for 2-BE (see Example 1). Analogous health-based standards are not available for 2-HE (e.g., see the National Library of Medicine's listing: : <http://toxnet.nlm.nih.gov/cgi-bin/sis/search/r?dbs+hsdb:@term+@rn+112-25-4>; accessed on Jan. 16, 2006).

As shown in Figure 3.5 (Experiment 1L) the actual concentrations of 2-BE and 2-HE during the cleaning are expected to be lower than these "idealized" concentrations, where "idealized" refers to calculated values for release of an inert tracer into a well-mixed indoor air volume ventilated at a constant rate. The difference is due primarily to sorption processes. However, the concentrations of 2-BE and 2-HE are also expected to remain elevated for at least 24 hours after the end of the cleaning event owing to re-emission (see middle panel of Figure 3.5).

5.1.5. Example 5: Air freshener and ozone in a child's bedroom

Although ill advised, some people who are concerned about air quality and odors in their child's bedroom, and influenced by false or misleading advertising, might choose to use both air fresheners and ozone-generating devices simultaneously in such rooms.

In this example consider a 50-m^3 bedroom, ventilated at 1 h^{-1} , containing both a plug-in air freshener and an ozone-generating device (either an advertised ozone generator or an ion generator that also produces ozone) that is responsible for a residual ozone concentration averaging 50 ppb. The 50-m^3 chamber experiments reported in §4.4-4.5 indicate that, at the same air-exchange rate, the simultaneous presence of an air freshener and 50 ppb of residual ozone (Figure 4.9d, Expt. 3K) resulted in a steady-state increase in formaldehyde concentration of ~ 6 ppb (see Table 4.11 and text in Section 4.5.4). Assume that the child sleeps in the bedroom 9 hours/day and spends an additional, moderately active three hours per day playing in the bedroom. Then the child's formaldehyde exposure resulting from ozone-initiated reactions with the constituents of this particular air freshener is ~ 70 ppb-h daily or $\sim 26,000$ ppb-h annually. Assuming a breathing rate of $0.45 \text{ m}^3 \text{ h}^{-1}$ while sleeping and $0.95 \text{ m}^3 \text{ h}^{-1}$ while playing, the child's formaldehyde intake resulting solely from the use of the air freshener in the presence of ozone is $\sim 50 \text{ } \mu\text{g d}^{-1}$. This exceeds California's "no significant risk level" (NSRL) for formaldehyde of $40 \text{ } \mu\text{g d}^{-1}$.

This example was predicated upon the use of AFR-1. Different air fresheners have different constituents. The ozone-reactive constituents, primarily the terpenoids, vary with the scent of the air freshener. It is instructive to compare the ingredients in AFR-1 with the ingredients identified by Liu et al. (2004) in a pine-scented, plug-in air freshener (see Fig. 1 of

their paper). Liu et al. measured a maximum formaldehyde concentration of approximately 20 ppb in the presence of 60 ppb residual ozone. However, both their chamber volume (30 m^3) and air-exchange rate (0.55 h^{-1}) were smaller than the respective parameters in the present study. Emission rates of terpenoids also vary from plug-in to wick-type to diffusion-type air fresheners. For some products it is anticipated that the resultant formaldehyde production and subsequent exposure will be larger than that resulting from the use of AFR-1 or the pine-scented air freshener examined by Liu et al.

In considering this example, it is important to remember that the formaldehyde generated by the ozone/air freshener chemistry will be added to formaldehyde emitted into the room from other sources (e.g., furniture, plywood and other pressed wood products, fiberglass insulation, etc.). The estimated daily intake of $\sim 50 \mu\text{g d}^{-1}$ is that which would result if there were no other sources of formaldehyde in the bedroom. In reality, this is unlikely to be the case.

5.1.6. Example 6: Cleaning when outdoor ozone levels are high

Another example illustrating the potential influence of reactive chemistry involves cleaning with a product such as GPD-1 during a period when the outdoor ozone levels are high.

Consider an apartment in Southern California on a day when the mid-afternoon outdoor ozone concentration is close to 120 ppb. Assume that the apartment is ventilated at 1 h^{-1} and that 3.7 g of GPD-1 are sprayed onto a greasy stovetop (1.2 ft^2 or 0.11 m^2) in a 50-m^3 kitchen. These conditions match those of Experiment 3C (Table 4.7). The reaction of ozone with the limonene present in GPD-1 results in a large increase in the concentration of $\text{PM}_{1.1}$ (see Figure 4.10 and Table 4.12). One hour after cleaning, the concentration of $\text{PM}_{1.1}$ in the kitchen is $180 \mu\text{g m}^{-3}$ and two hours after cleaning the $\text{PM}_{1.1}$ nears its maximum value of $275 \mu\text{g m}^{-3}$.

If the apartment dweller remains in the kitchen for two hours after cleaning the stovetop (e.g., working at the kitchen table), then his or her exposure to SOA from this simple cleaning procedure is approximately $320 \mu\text{g m}^{-3} \text{ h}$. If the occupant's breathing rate is $0.6 \text{ m}^3 \text{ h}^{-1}$ during this period, the resulting inhalation intake of SOA is approximately 190 μg . This 2-h intake is about two-thirds of the average daily intake experienced by the domestic cleaner in Example 2 and is approximately one-fourth the daily intake of $\text{PM}_{2.5}$ that would correspond to exposure at the NAAQS level of $65 \mu\text{g m}^{-3}$ (see Example 1 and the caution that $\text{PM}_{2.5}$ and SOA are not equivalent).

5.1.7. Example 7: Use of cleaning agents with elevated ozone and NO_2 levels

The simultaneous presence of ozone and nitrogen dioxide can generate meaningful concentrations of the nitrate radical (Weschler et al., 1992; Sarwar et al., 2002a). As can be seen from Table 2.8, the nitrate radical reacts rapidly with many of the known constituents of cleaning products and air fresheners.

A scenario that deserves special attention in this context is cleaning in a kitchen while cooking with a gas-fired appliance on a high-ozone day. Assume that the byproducts of gas combustion are vented into the indoor air, rather than being exhausted through a range hood. Assume that a kitchen window is partially open, admitting the elevated outdoor ozone level at a high rate. Assume that the outdoor ozone level is 100 ppb, the NO_2 concentration in the kitchen is 100 ppb and one or more of the kitchen cleaning activities outlined in Table 5.1 is being conducted.

Unfortunately, we lack sufficient information to carry this exercise to conclusion. The nitrate radical concentration can be estimated from mass balance models (Sawar et al., 2002a),

but accurate estimates require accounting for all of the sinks in this scenario, something that is difficult to do with confidence. Even with an estimated nitrate radical concentration, the products (and yields) of nitrate radicals reacting with common constituents of cleaning products are poorly defined. This is especially true for the nitrated organics. A recent study conducted at UC Riverside (Gong et al., 2005) used thermal desorption particle beam mass spectrometry to examine the constituents of SOA formed via the reaction of nitrate radicals with simple alkenes. The identified first-generation products include hydroxynitrates, carbonylnitrates, nitrooxy peroxy nitrates, dihydroxynitrates, and dihydroxy peroxy nitrates, while the second-generation products include hydroxy and oxo dinitrooxytetrahydrofurans, neither of which have been previously reported. Such nitrated organics are of particular interest, given the fact that related nitrated organics are known carcinogens (Gupta et al., 1996). Although the Gong et al. study focused on simple alkenes, one would expect analogous product formation for many of the unsaturated species listed in Table 2.7 (known constituents of cleaning products and air fresheners with carbon-carbon double bonds). Furthermore, given the molecular weight of most of the compounds in Table 2.7, many of the products are anticipated to have low volatilities and contribute to SOA production. This is an area that requires additional detailed experimental study to better define the products formed and their yields as a basis to estimate exposures and intakes.

5.1.8. *Summary of the scenario results*

Table 5.3 summarizes key findings from the seven examples considered here.

5.2. Limitations: Chemistry and toxicology

5.2.1. *Stealth products of ozone-initiated chemistry*

The previous examples involving exposures to air pollutants generated by reactive chemistry have focused on oxidation products that were identified and quantified in both the small and large chamber experiments presented in §4 of this report. However, a number of the products of ozone-initiated chemistry are difficult or impossible to detect and quantify using routine analytical methods (Weschler and Shields, 1997; Wolkoff et al., 1997). A good example involves the reaction between ozone and linalool, a constituent of AFR-1. In experiments 3J and 3K (Table 4.7), air freshener AFR-1 had been in the 50-m³ chamber for several hours before realistic levels of ozone were introduced into the supply air. During the first hour after ozone was introduced, the concentration of linalool decreased by 37 µg m⁻³. Less than 4% of this decrease was due to a decreasing emission rate; the majority of the decrease was due to reaction with ozone and concomitant production of oxidation products. Shu et al. (1997) used several analytical methods, including direct air sampling atmospheric pressure ionization-tandem mass spectrometry (API MS/MS) and Fourier transform infrared absorption spectroscopy, to examine the products formed when ozone reacts with linalool. They report the following products and yields: formaldehyde (36%), acetone (21%); 4-hydroxy-4-methyl-5-hexen-1-al (85%) and 5-ethenyl-dihydro-5-methyl-2(3H) furanone (13%). These results indicate that the ozone/linalool reaction in Experiments 3J and 3K is anticipated to produce, during the 1st hour, about 30 µg m⁻³ of 4-hydroxy-4-methyl-5-hexen-1-al, the complementary product in the attack of the double bond that produces acetone, and about 5 µg m⁻³ of 5-ethenyl-dihydro-5-methyl-2(3H) furanone. However, neither of these products was detected in the current study. This is not surprising as direct air sampling atmospheric pressure ionization-tandem mass spectrometry and Fourier transform infrared absorption spectroscopy can detect compounds that are not adequately sampled or recovered by standard GC/MS methods.

This is just one example of a situation where oxidation products are anticipated to be present, but are not readily detected by sorbent sampling followed by TD-GC/MS. For many of the terpenoids used in cleaning products or air fresheners, the pathway that produces formaldehyde or acetone also produces a complementary carbonyl that is not readily detected by routine analytical methods. Although such compounds may escape detection, they contribute to the total exposure of humans present in environments where such chemistry occurs.

5.2.2. Lack of toxicological data for oxidation products

Toxicological data exist for most of the primary constituents identified in this report. Although more toxicological data are desirable for some of these compounds (this is a goal of EPA's HPV program – see <http://www.epa.gov/chemrtk/volchall.htm>), at a minimum toxicologists have consciously considered the constituents in terms of their potentially adverse effects on human health. However, as is apparent from §4 of this report, exposures resulting from the use of cleaning products and air fresheners include exposures to chemically transformed constituents. The toxicological properties of a few of the products resulting from oxidation of constituents of cleaning products and air fresheners have been extensively investigated (e.g., formaldehyde, acetaldehyde, acetone). For other products, toxicological properties may not have been thoroughly investigated, but a specific adverse effect for linalool has been identified. Skold et al. (2002) have shown that the hydroperoxides formed when O₂ reacts with linalool are potent contact allergens. However, toxicological properties have not been evaluated for many of the products formed when ozone, hydroxyl radicals or nitrate radicals react with cleaning product and air freshener constituents. This is especially true for the condensable oxidization products that constitute secondary organic aerosols.

5.2.3. Knowledge gaps

In evaluating the consequences of exposure to both primary and secondary pollutants from cleaning products and air fresheners a number of knowledge gaps are apparent, as recorded here. 1) Rate constants are missing for reactions between various constituents and O₃, OH and NO₃. 2) Many of the oxidation products resulting from reactions between various constituents and O₃, OH and NO₃ remain unidentified or un-quantified. This is especially so for products resulting from nitrate radical reactions. 3) Toxicological data are sparse or nonexistent for many oxidation products. 4) Information is lacking regarding sorption/desorption parameters for constituents and oxidation products to various real world surfaces 5) Information is lacking regarding the influence of sorption on the chemical transformation of constituents.

As these knowledge gaps are closed, the exposures to primary and secondary pollutants resulting from the use of cleaning products and air fresheners will become better defined, and the ability to make connections between such exposures and adverse health effects will improve.

5.3. Practical measures to reduce exposures

Ozone concentrations lower than those known to produce adverse health effects (e.g., 120 ppb for 1 h and 80 ppb for 8 h, as justified in the supporting material for the current NAAQS) can still drive significant indoor chemistry, generating oxidation products at rates large enough to result in meaningful concentrations of oxidation products. This is apparent from §4 of the current report. It is prudent to avoid the use of products with ozone-reactive constituents in situations where the indoor ozone concentrations are moderate to high (> 20 ppb). In the presence of ozone

generating devices, people should definitely avoid the use of cleaning products or air fresheners containing ozone-reactive compounds.

The following simple measures can reduce individual inhalation exposures to the constituents of cleaning products and their chemical transformation products.

- (1) Follow the instructions for use. Do not use more of the cleaning agent than is necessary to complete the job.
- (2) Rinse surfaces; remove paper towels, sponges and mops; rinse sponges and mops before storing.
- (3) Use adequate ventilation during cleaning.
- (4) Keep the ventilation rate high for several hours after cleaning (extended desorption of sorbed primary constituents and their reaction products).
- (5) Avoid cleaning with products that have reactive constituents on days when the outdoor ozone levels are high.
- (6) Avoid the use of ozone generators or ionizing air cleaners, especially in the same space with cleaning products or air fresheners that contain reactive constituents.

Table 5.1. Estimated annual inhalation intake of 2-butoxyethanol (2-BE), formaldehyde (HCHO), and secondary organic aerosol (SOA) for occupant of home or large apartment who does her/his own cleaning.

Activity	Product	F (d/y) ^a	Duration (h)		Inhalation intake (mg/y)		
			Activity	Exposure	2-BE	HCHO	SOA
Counter wiping ^b	GPC-3	365	0.25	2	580		
Counter cleaning ^b	GPC-3	48	0.5	2	185		
Kitchen floor mopping ^{b, c}	GPC-1	48	0.65	4		1.3	3.7
Bathroom floor mopping ^{b, d}	GPC-1	48	0.42	0.42		0.3	0.8
Bathroom ^b	GPC-2	24	0.67	0.67	28		
Appliances ^{b, e}	GPC-1	48	0.56	2		1.3	6.1
Interior windows ^b	GLC-1	4	4.5	12	120		
Other glass surf. ^{b, f}	GLC-1	48	0.71	2	130		
Cabinets ^b	GPC-3	12	1.75	2	46		
Walls & doors ^{b, g}	GPC-1	12	1.58	4		0.4	1.2
Oven	GPC-3	2	0.5	2	4		
Air freshener ^h	AFR-1	365	na	18		4.5	1.1
Total annual inhalation intake (mg/y)					1100	8	13

^a Frequency of use, number of days per year.

^b Indicates that values for the frequency of the activity and its duration come from the mean values in the USEPA's Exposure Factors Handbook

^c Concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; floor area (15.6 m²) assumed to be four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

^d Concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; two full bathrooms with total floor area (15.6 m²) four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

^e Stove, refrigerator, dishwasher: concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for simulated cleaning of a cook top; appliance surfaces (0.44 m²) four times larger than 0.11 m² used in chamber, but [O₃] assumed to be four times smaller.

^f Mirrors, table tops, picture frames: assume room loading 1/4 of window interior surfaces.

^g Clean with same dilution of GPC-1 as used on floors; resulting concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; wall and door area (15.6 m²) four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

^h Concentrations reduced to 1/6 of those reported in Tables 4.11 (HCHO) and 4.12 (SOA) since [O₃] assumed to be six times smaller than in the 50 m³ chamber experiments.

Table 5.2. Annual estimated inhalation intake of 2-butoxyethanol (2-BE), formaldehyde (HCHO), and secondary organic aerosol (SOA) for person employed as a domestic cleaner.

Activity	Product	F (d/y) ^a	Duration (h)		Inhalation intake (mg/y)		
			Activity	Exposure	2-BE	HCHO	SOA
Counter cleaning ^b	GPC-3	250	0.5	2.5	1,960		
Kitchen floor moppng ^{b, c}	GPC-1	250	1.5	2.5		9.1	26
Bathroom floor mopping ^{b, d}	GPC-1	250	0.5	0.5		1.8	5
Bathroom ^b	GPC-2	250	1.5	1.5	650		
Appliances ^{b, e}	GPD-1	250	0.5	2.5		16	73
Interior windows ^b	GLC-1	40	4.5	4.5	1,160		
Other glass surf. ^{b, f}	GLC-1	250	0.5	2	1,130		
Cabinets ^b	GPC-3	60	1.75	2	243		
Walls & doors ^{b, g}	GPC-1	60	1	2		1.8	5
Oven	GPC-3	20	0.5	2	69		
Total annual inhalation intake (mg/y)					5,200	29	109

^a Frequency of activity and exposure, number of days per year.

^b Indicates that values for the frequency of the activity and its duration come from the mean values in the USEPA's Exposure Factors Handbook

^c Concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; floor area (15.6 m²) assumed to be four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

^d Concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; two full bathrooms with total floor area (15.6 m²) four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

^e Stove, refrigerator, dishwasher: concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for simulated cleaning of a cook top; appliance surfaces (0.44 m²) four times larger than 0.11 m² used in chamber, but [O₃] assumed to be four times smaller.

^f Mirrors, table tops, picture frames: assume room loading 1/4 of window interior surfaces.

^g Clean with same dilution of GPC-1 as used on floors; resulting concentrations the same as those reported in Tables 4.11 (HCHO) and 4.12 (SOA) for floor mopping; wall and door area (15.6 m²) four times larger than 3.9 m² used in chamber, but [O₃] assumed to be four times smaller.

Table 5.3. Key findings from illustrative exposure scenarios related to cleaning product and air freshener use.^a

Scenario	Key Finding
1. Routine cleaning by occupant	Average daily inhalation intake of 3.0 mg d ⁻¹ (3000 µg d ⁻¹) for 2-BE, 21 µg d ⁻¹ for HCHO and 35 µg d ⁻¹ for SOA.
2. Multi-house cleaning by professional domestic cleaner	Average daily inhalation intake of 14.0 mg d ⁻¹ (14,000 µg d ⁻¹) for 2-BE, 80 µg d ⁻¹ for HCHO and 300 µg d ⁻¹ for SOA.
3. Cleaning in a small, moderately ventilated bathroom	First hour gas-phase concentration for 2-BE of 177 mg m ⁻³ (37,000 ppb); inhalation intake of 2-BE during 15 minute cleaning event is approximately 60 mg.
4. Whole-house interior window cleaning	Initial 2-hour gas-phase concentration for 2-BE of 17 mg m ⁻³ for 2-BE and 10 mg m ⁻³ for 2-HE; inhalation intake of 2-BE during 2-hour cleaning event is 45 mg, and intake of 2-HE is 27 mg.
5. Air freshener and ozone-emitting air cleaner in a child's bedroom	Child's inhalation intake of formaldehyde resulting solely from the use of an air freshener in the presence of ozone is ~ 50 µg d ⁻¹ .
6. Cleaning when outdoor ozone levels are high	Inhalation intake of SOA over a 2-hour period that includes cleaning and post-cleaning exposure is approximately 190 µg.
7. Use of cleaning agents with elevated nitrogen dioxide from a gas range and elevated ozone from outdoors	Nitrogen dioxide and ozone react to generate nitrate radicals, which react rapidly with many of the known constituents of cleaning products and air fresheners. However, there is insufficient information to carry this exercise to conclusion.

^a Standards and guidelines for assessing exposure to 2-butoxyethanol (2-BE), formaldehyde (HCHO), and secondary organic aerosol (SOA):

- 2-BE: California has established an acute one-hour exposure limit of 14 mg m⁻³ for 2-BE (OEHHA, 1999). For a breathing rate of 1.3 m³ h⁻¹, exposure at this level would result in an intake of 18 mg during one-hour of exposure. The federal reference concentration (RfC) for chronic inhalation exposure is 13 mg m⁻³ (<http://www.epa.gov/iris/subst/0500.htm>). Assuming that an adult inhales between 12 and 15 m³ of air a day, exposure at this level is equivalent to a daily inhalation intake of 156-195 mg.
- HCHO: California's "no significant risk level" (NSRL) for formaldehyde intake is 40 µg d⁻¹ based on the inhalation exposure inferred to cause cancer (OEHHA, 2003). The chronic reference exposure level for formaldehyde in California is 2 ppb (http://www.oehha.ca.gov/air/chronic_rels/pdf/50000.pdf).
- SOA: The 24-h national ambient air quality standard for PM_{2.5} is 65 µg m⁻³. Given that the typically adult inhales between 12 and 15 m³ of air a day, this is equivalent to a daily intake of 780-975 µg. However, PM_{2.5} and SOA are not equivalent. Additional standards for ambient PM that might be considered are the annual-average federal PM_{2.5} standard of 15 µg m⁻³, the California standard for 24-h average PM₁₀ of 50 µg m⁻³, and the California standard for annual average PM_{2.5} levels of 12 µg m⁻³. See text for further discussion.

6. SUMMARY AND CONCLUSIONS

Although not widely recognized, chemical transformations do occur in indoor air. Such transformations influence the kinds and amounts of pollutants to which people are exposed, and therefore alter source-oriented health risks. Air pollution sources are regulated largely because of concern about the health risks associated with human inhalation exposures. In regulating sources that emit to ambient air, it is now well known that one must recognize the potential for chemical transformations and account for their significance.

An analogy can be drawn between products and processes that emit pollutants into urban atmospheres and those that emit into indoor air. Consider the case of motor vehicle emissions into urban air. Pollutants directly emitted are termed primary emissions. For motor vehicles, these include unburned and partially oxidized fuel constituents, nitrogen oxides from high-temperature combustion, carbon monoxide from fuel-rich combustion conditions, and particulate matter both from the tail pipe and from abrasive wear of brakes, tires, and road surfaces. Adverse health consequences can result from exposure to these primary pollutants. In the atmosphere, certain primary pollutants can also undergo transformations. Nitrogen oxides and volatile organic compounds combine in the presence of sunlight to form a suite of secondary pollutants, among which are ozone, hydrogen peroxide, peroxyacetyl nitrate, aldehydes, organic and inorganic acids, and secondary particulate matter. Exposure to these species also can pose serious risks of adverse health consequences. Thus, if one seeks to understand the health risks associated with motor vehicle use, one must not only consider the primary emissions, but also the formation of secondary pollutants.

Evidence is emerging that the same principle applies for indoor environments. Source-oriented health risks are not solely a consequence of primary emissions, but may also have important contributions from secondary pollutants.

The activity of cleaning in indoor environments generates benefits by improving aesthetics and hygiene, and by preserving objects. Cleaning also generates risks, including the inhalation of volatile constituents of cleaning products or of secondary pollutants formed by reactive chemistry. The benefits of air fresheners are more subjective, while the risks parallel those associated with cleaning. Studies have documented adverse health outcomes that are associated with inhalation exposure to cleaning activities or with exposure to cleaning product constituents. For example, several recent studies indicate an increased incidence of occupational asthma in those employed as cleaners. However, causative agents remain to be identified. A better understanding of inhalation exposures to primary and secondary pollutants owing to cleaning product and air freshener use should ultimately lead to diminished risks while expanding the benefits derived from them.

The research reported here contributes to efforts to better understand human exposures to both primary and secondary pollutants associated with cleaning product and air freshener use. The project began with a thorough review of the literature. To the extent that they occur, inhalation risks from cleaning-product use begin with emissions, and emissions begin with product composition. Challenges arise because some of the desirable attributes of a cleaning-product's active ingredients are also attributes of chemicals that are irritating or otherwise pose health risks. Surfactants, acids, bases, oxidants, complexing agents, and solvents are used in specific cleaning products because they facilitate that product's function. Choices can and have been made to select compounds that are less toxic for these functions. Fragrances are inherent to air fresheners and may improve the aesthetic character of a cleaning product. A challenge is to employ fragrances that are less likely to produce hazardous secondary products. Ultimately,

inhalation exposures that result from the use of cleaning products and air fresheners are governed by the complex interplay of three sets of factors: those that govern chemical emissions from the product; those that influence the dynamic behavior of the species in the indoor environment; and the human factors related to product use, building operation, and occupancy. The literature review indicates that current understanding is sufficient to describe the influence of these variables qualitatively in most cases and quantitatively in a few.

A suite of experiments was designed and executed to investigate the composition, emissions, and concentrations of primary constituents and secondary species associated with a set of cleaning products and air fresheners. The experimental research focused on widely available consumer products marketed for household cleaning or as air fresheners. Attention ultimately focused on two classes of chemicals. Ethylene-based glycol ethers were studied because of their prominence as solvents in cleaning products and because this class of compounds is regulated as toxic air contaminants (TAC) by the State of California. Terpenes are a class of volatile organic compounds derived from plants. They are widely used in consumer products, including many cleaning products and air fresheners, owing to their effective solvent properties and their pleasant smell. Many terpenes and related compounds react rapidly with ozone. Among the reaction byproducts are aldehydes, the hydroxyl radical, and secondary particulate matter.

To guide the selection of specific products for the experimental research, a shelf survey was conducted at five major retail stores in the East Bay of the San Francisco Bay Area. A total of 291 distinct consumer products for cleaning or air freshening were found at these stores. Twenty-one of these were selected for chemical screening because they were widely available, were likely to contain compounds from one or both target classes, and because they collectively represented a broad range of product categories. Volatile components of the products were measured. Six of the 21 products contained significant quantities ($> 0.01\%$) of the glycol ethers, 2-butoxyethanol (in six products) and 2-hexyloxyethanol (in one product), with total glycol ether mass fractions ranging from 0.8 to 9.6%. Twelve of the 21 products contained significant quantities ($> 0.05\%$) of ozone-reactive compounds — i.e., terpene hydrocarbons and other unsaturated oxygenated compounds — with mass fractions ranging from 0.2 to 26%. One product contained substantial amounts of both 2-butoxyethanol (1.7%) and ozone-reactive compounds (3.9%) and only four of the 21 products contained very low levels of both classes of compounds.

With this information in hand, seven products were selected for further experimental investigation. For six products, eighteen simulated-use experiments were conducted in a controlled, room-sized experimental chamber. The goal of these experiments was to measure emissions and concentrations of target compounds that would result from high, but realistic use of these products in an indoor setting. For three products (two repeated from the prior phase and one distinct), further experiments were conducted to investigate the reactive chemistry between cleaning product and air freshener constituents and ozone. Two sets of experiments were carried out: fifteen in a bench-scale (198-L) chamber and eleven involving simulated use.

The experimental results provide information that is directly relevant to emissions and resulting gas-phase concentrations of glycol ethers (primary pollutants) and terpenes that may react with ozone to form secondary pollutants. Simplified modeling of cleaning scenarios using the emission factors determined in this study indicates that peak 1-h exposure concentrations for 2-butoxyethanol might approach or potentially exceed California's acute reference exposure level of 14 mg m^{-3} in some situations. Limonene and other ozone-reactive terpenoids present in

cleaning products can reach mg m^{-3} levels in air and persist at levels of tens to hundreds of $\mu\text{g m}^{-3}$ for many hours after cleaning. Air fresheners can produce steady-state levels of tens to hundreds of $\mu\text{g m}^{-3}$ of ozone-reactive terpenoids.

The use of terpene-containing cleaning products, combined with ambient ozone entering by means of ventilation, can produce significant quantities of secondary air pollutants. Specifically, both formaldehyde (itself a toxic air contaminant) and fine particle mass are generated in quantities that, combined with other common indoor sources, may result in exposures exceeding relevant health-based standards and guidelines under some circumstances. Also, both ozone and OH may generate “stealth” products that cannot be measured with the methods employed here, but nevertheless raise potential health concerns.

While effective cleaning can improve the healthfulness of indoor environments, this work shows that use of some consumer cleaning agents can yield high levels of air pollutants, including glycol ethers, formaldehyde, and particulate matter. Persons involved in cleaning, especially those who clean occupationally or often, might encounter excessive exposures to these pollutants owing to cleaning product emissions. The research reported here suggests some simple measures that can be employed to reduce exposures to primary and secondary pollutants associated with cleaning products and air fresheners. Use products in dilute form whenever appropriate. Do not use more of the cleaning agent than is necessary to complete the job. Clean during periods of low occupancy, and allow adequate time for removal by ventilation before the space is heavily occupied. Use adequate ventilation during and for several hours following cleaning. Rinse surfaces; remove paper towels, sponges and mops from the cleaned area; rinse sponges and mops before storing. Don’t use products with ozone-reactive constituents on days when outdoor ozone levels are high. Avoid the use of ozone generators or ionizing air cleaners, especially in the presence of cleaning products and air fresheners that contain ozone-reactive constituents.

7. RECOMMENDATIONS

It is broadly recognized that air pollution problems are best controlled at the source. However, this project helps bring into focus two other important points that have not been so broadly recognized in air quality management. First, in assessing the relative significance among different sources contributing to human exposure, *proximity* between source and receptor is an extremely important determinant (Smith, 2002). The *rule of 1000* states that the release of a gram of a pollutant into indoor air causes as much inhalation exposure as the release of a kilogram into ambient air (Smith, 1988). Emissions from cleaning products and air fresheners contribute in a relatively minor way to ambient concentrations of volatile organic compounds (VOC). However, they may contribute in a substantial way to human inhalation intake to VOC, because most of the emissions occur in close proximity to people in indoor environments. When household products contain chemicals that are classified as toxic air contaminants (TAC), then the potential for human exposure to those chemicals should be assessed. The research reported here demonstrates that inhalation exposure to ethylene-based glycol ethers owing to their presence in cleaning products can reach consequential levels in relation to health-based guidelines.

The second important point elucidated by this research is that reactive chemistry in indoor air can have an important influence on the nature and concentrations of air pollutants to which people are exposed. Several factors combine to raise concern: the common presence of terpenes and related compounds in cleaning products and air fresheners; the elevated levels of ozone in the urban and regional troposphere; the introduction of ozone into buildings by means of ventilation, or directly from indoor sources; the rapid reactivity of terpenes with ozone; and the significant production of secondary pollutants owing to ozone-terpene chemistry. The research reported here has focused on the generation of formaldehyde, the hydroxyl radical, and fine particulate matter, and has demonstrated that the levels of these secondary products in association with ordinary indoor conditions are high enough to warrant additional investigation.

Given these broad considerations, and in light of the specific findings of the present project, we suggest three additional research topics that might be fruitfully pursued.

The first topic is to better characterize *exposures* to primary and secondary pollutants that result from the use of cleaning products and air fresheners indoors. The present project was designed to emphasize conditions that would produce indoor concentrations that are elevated, but within a realistic range. The work has demonstrated the potential for significant indoor concentrations to be generated of primary glycol ethers, such as 2-butoxyethanol, and pollutants such as formaldehyde and particulate matter. It would be worthwhile to further investigate exposures to Californians that occur via this source. This work could be pursued by means of modeling or measurement. Key data needs include better information on human factors that affect use and exposure. A goal could be to seek to quantify the distribution of exposures among the California population to glycol ethers, secondary formaldehyde, and secondary particulate matter owing to the use of cleaning products and air fresheners. Alternatively, attention could be focused on characterizing exposures to subpopulations of concern, such as those occupationally exposed as cleaners, those with preexisting respiratory health conditions, such as asthma, or the very young.

A second topic that merits further study is indoor reactive chemistry. There are several specific lines of inquiry that are suggested by the results of this project. First, additional investigation of the dynamics of secondary particle formation owing to indoor reactive chemistry between ozone and terpenes merits further consideration. What factors control whether

nucleation or condensational growth will occur? In ordinary indoor environments, what is the size distribution and chemical composition of particles that result from this process? Second, further investigation of the role of surface chemistry involving constituents of cleaning products and air fresheners appears warranted. The bench-scale chamber experiments that demonstrated particle nucleation events triggered by ozone reactions with nonvolatile product residues on a surface are intriguing and raise the question of whether such processes also occur in ordinary indoor environments. Third, the consequences of hydroxyl radical formation for indoor reactive chemistry merit further consideration. Indoor environments typically contain complex mixtures of VOC, and the production of the OH radical by ozone-terpene chemistry can trigger additional transformations that could significantly influence the nature and concentrations of air pollutants (Fan et al., 2003). Fourth, additional research investigating nitrate radical reactions with cleaning product and air freshener constituents is warranted. The limited work done in this project (experiment 2O) indicates that the simultaneous presence of ozone and nitrogen dioxide, which generates the nitrate radical, does affect indoor reactive chemistry. The literature review clearly indicates that nitrate radicals can react rapidly enough with certain unsaturated constituents of cleaning products and air fresheners to matter (Table 2.8). Finally, additional effort is warranted to measure “stealth” chemicals in indoor air, i.e. those species that are expected to be formed, but are not measured because of their short-lived nature, or because of challenges in sampling and analysis. Sophisticated experimental techniques have been developed to study such chemicals in laboratory systems, and the potential exists to apply some of these techniques in field settings to better characterize the products of indoor reactive chemistry.

The third topic that warrants investigation is the health consequences associated with cleaning product and air freshener use. Specifically, studies appear warranted to investigate whether a causal connection exists between occupational employment as a cleaner and occupational asthma. If so, additional efforts would be merited to determine the causative agents. Also, work could fruitfully be pursued to investigate whether exposure to primary constituents or secondary products of cleaning products and air fresheners might be associated with exacerbation of asthma among those who are more susceptible. Studies that seek to directly characterize the potential adverse health consequences of secondary particulate matter formed from indoor reactive chemistry appear worthwhile. The association has been well documented between elevated ambient ozone and adverse health consequences. The cause of this association is not understood. It has been suggested that ozone-initiated indoor chemistry may be more directly responsible for this association than the direct exposure to outdoor ozone (Weschler, 2004b). By demonstrating the substantial degree to which secondary pollutants can be formed by ozone-terpene chemistry, the present study provides further evidence supporting the plausibility of this hypothesis. Removing ozone from ventilation air is readily accomplished using activated carbon filters. This raises the possibility of conducting an intervention study to test the hypothesis that ozone-induced indoor reactive chemistry adversely affects human health.

References

- Adams WC, 1993. Measurement of breathing rate and volume in routinely performed daily activities. Final Report Contract No. A033-205, Air Resources Board, California Environmental Protection Agency, Sacramento, CA.
- Akland G, Whitaker DA, 2000. Characterizing the sources of human exposure to Proposition 65 substances. RTI/6830/02-03 F, Research Triangle Institute, Research Triangle Park, NC.
- Alvarado A, Tuazon EC, Aschmann SM, Arey J, Atkinson R, 1999. Products and mechanisms of the gas-phase reactions of OH radicals and O₃ with 2-methyl-3-buten-2-ol. *Atmospheric Environment* 33, 2893-2905.
- An Y, Zhang JS, Shaw CY, 1999. Measurements of VOC adsorption/desorption characteristics of typical interior building materials. *HVAC & R Research* 5, 297-316.
- Arif AA, Delclos GL, Whitehead LW, Tortolero SR, Lee ES, 2003. Occupational exposures associated with work-related asthma and work-related wheezing among US workers. *American Journal of Industrial Medicine* 44, 368-376.
- Aschmann SM, Martin P, Tuazon EC, Arey J, Atkinson R, 2001. Kinetic and product studies of the reactions of selected glycol ethers with OH radicals. *Environmental Science & Technology* 35, 4080-4088.
- Aschmann SM, Arey J, Atkinson R, 2002. OH radical formation from the gas-phase reactions of O₃ with a series of terpenes. *Atmospheric Environment* 36, 4347-4355.
- Atkinson R, Aschmann SM, Pitts Jr JN, 1986. Rate constants for the gas-phase reactions of the OH radical with a series of monoterpenes at 294 ± 1 K. *International Journal of Chemical Kinetics* 18, 287- 299.
- Atkinson R, Aschmann SM, 1988. Kinetics of the reactions of acenaphthene and acenaphthylene and structurally-related aromatic compounds with OH and NO₃ radicals, N₂O₅ and O₃ at 296 ± 2 K. *International Journal of Chemical Kinetics* 20, 513-539.
- Atkinson R, Aschmann SM, Arey J, 1990a. Rate constants for the gas-phase reactions of OH and NO₃ radicals and O₃ with sabinene and camphene at 296 ± 2 K. *Atmospheric Environment* 24, 2647- 2654.
- Atkinson R, Hasegawa D, Aschmann SM, 1990b. Rate constants for the gas-phase reactions of O₃ with a series of monoterpenes and related compounds at 296 ± 2 K. *International Journal of Chemical Kinetics* 22, 871-887.
- Atkinson R, 1991. Kinetics and mechanisms of the gas-phase reactions of the NO₃ radical with organic compounds. *Journal of Physical and Chemical Reference Data* 20, 459-507.
- Atkinson R, Arey J, Aschmann SM, Corchnoy SB, Shu Y, 1995. Rate constants for the gas-phase reactions of cis-3-hexen-1-ol, cis-3-hexenylacetate, trans-2-hexenal, and linalool with OH and NO₃ radicals and O₃ at 296 ± 2 K, and OH radical formation yields from the O₃ reactions. *International Journal of Chemical Kinetics* 27, 941-955.
- Atkinson R, 1997. Gas-phase tropospheric chemistry of volatile organic compounds 1. Alkanes and alkenes. *Journal of Physical and Chemical Reference Data* 26, 215-290.
- Atkinson R, Arey J, 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: A review. *Atmospheric Environment* 37 (supplement 2), 197-219.
- Baughman AV, Gadgil AJ, Nazaroff WW, 1994. Mixing of a point source pollutant by natural convection flow within a room. *Indoor Air* 4, 114-122.
- Bekö G, Halás O, Clausen G, Weschler CJ, 2006. Initial studies of oxidation processes on filter surfaces and their impact on perceived air quality. *Indoor Air* 16, 56-64.

- Bennett DH, McKone TE, Evans JS, Nazaroff WW, Margni MD, Jolliet O, Smith KR, 2002. Defining intake fraction. *Environmental Science & Technology* 36, 206A-211A.
- Bennion JR, Franzblau A, 1997. Chemical pneumonitis following household exposure to hydrofluoric acid. *American Journal of Industrial Medicine* 31, 474-478.
- Betts K, 2003. Are U.S. homes a haven for toxins? *Environmental Science & Technology* 37, 407A-411A.
- Bloomfield SF, Scott E, 1997. Cross-contamination and infection in the domestic environment and the role of chemical disinfectants. *Journal of Applied Microbiology* 83, 1-9.
- Bodalal A, Zhang JS, Plett EG, 2000. A method for measuring internal diffusion and equilibrium partition coefficients of volatile organic compounds for building materials. *Building and Environment* 35, 101-110.
- Bodin A, Fischer T, Bergh M, Nilsson JLG, Karlberg AT, 2000. Skin irritation from air-oxidized ethoxylated surfactants. *Contact Dermatitis* 43, 82-89.
- Bodin A, Shao LP, Nilsson JLG, Karlberg AT, 2001. Identification and allergenic activity of hydroxyaldehydes — A new type of oxidation product from an ethoxylated non-ionic surfactant. *Contact Dermatitis* 44, 207-212.
- Bodin A, Linnerborg M, Nilsson JLG, Karlberg AT, 2002. Novel hydroperoxides as primary autoxidation products of a model ethoxylated surfactant. *Journal of Surfactants and Detergents* 5, 107-110.
- Bodin A, Linnerborg M, Nilsson JLG, Karlberg AT, 2003. Structure elucidation, synthesis, and contact allergenic activity of a major hydroperoxide formed at autoxidation of the ethoxylated surfactant C12E5. *Chemical Research in Toxicology* 16, 575-582.
- Boeniger MF, 1995. Use of ozone generating devices to improve indoor air-quality. *American Industrial Hygiene Association Journal* 56, 590-598.
- Borrazzo JE, Davidson CI, Andelman JB, 1993. Small closed-chamber measurements for the uptake of trichloroethylene and ethanol vapor by fibrous surfaces, In Nagda NL (Ed.), *Modeling of Indoor Air Quality and Exposure*, ASTM STP 1205, American Society for Testing and Materials, Philadelphia, pp. 25-41.
- Bouhamra W, Elkilani A, 1999a. Development of a model for the estimation of indoor volatile organic compounds concentration based on experimental sorption parameters. *Environmental Science & Technology* 33, 2100-2105.
- Bouhamra WS, Elkilani AS, 1999b. Investigation and modeling of surface sorption/desorption behavior of volatile organic compounds for indoor air quality analysis. *Environmental Technology* 20, 531-545.
- Burge PS, Richardson MN, 1994. Occupational asthma due to indirect exposure to lauryl dimethyl benzyl ammonium-chloride used in a floor cleaner. *Thorax* 49, 842-843.
- Calogirou A, Larsen BR, Brussol C, Duane M, Kotzias D, 1996. Decomposition of terpenes by ozone during sampling on Tenax. *Analytical Chemistry* 68, 1499-1508.
- Calogirou A, Larsen BR, Kotzias D, 1999a. Gas-phase terpene oxidation products: A review. *Atmospheric Environment* 33, 1423-1439.
- Calogirou A, Jensen NR, Nielsen CJ, Kotzias D, Hjorth J, 1999b. Gas-phase reactions of nopinone, 3-isopropenyl-6-oxo-heptanal, and 5-methyl-5-vinyltetrahydrofuran-2-ol with OH, NO₃, and ozone. *Environmental Science & Technology* 33, 453-460.
- CARB, 2001. The California Consumer Products Regulations. California Environmental Protection Agency Air Resources Board, Sacramento, CA.

- CARB, 2003. 1997 Consumer and Commercial Products Survey — Summary of Sales and Emissions (as of 3/21/00). California Air Resources Board, Sacramento, CA. Accessed at <http://www.arb.ca.gov/consprod/regact/ccps/ccps.pdf>.
- CARB, 2005a. Regulation for Reducing Volatile Organic Compound Emissions from Consumer Products, 2004 Amendments. California Air Resources Board, Sacramento, CA. February 10, 2005.
- CARB, 2005b. Indoor air pollution in California — Report to the California legislature. Principal Authors: Shimer D, Phillips TJ, Jenkins PL, California Air Resources Board, July 2005. <http://www.arb.ca.gov/research/indoor/ab1173/finalreport.htm>.
- Carrick RL, 1998. The Proposition 65 Handbook, 2nd Edition. American Environmental Institute, San Francisco.
- Carshaw N, 2003. New directions: Where next with indoor air measurements? *Atmospheric Environment* 37, 5451-5453.
- Chang JCS, Tichenor BA, Guo Z, Krebs KA, 1997. Substrate effects on VOC emissions from a latex paint. *Indoor Air* 7, 241-247.
- Chang JCS, Sparks LE, Guo Z, Fortmann R, 1998. Evaluation of sink effects on VOCs from a latex paint. *Journal of the Air & Waste Management Association* 48, 953-958.
- Chew AA, Atkinson R, Aschmann SM, 1998. Kinetics of the gas-phase reactions of NO₃ radicals with a series of alcohols, glycol ethers, ethers and chloroalkenes. *Journal of the Chemical Society — Faraday Transactions* 94, 1083-1089.
- Clausen PA, Wolkoff P, 1997. Degradation products of Tenax TA formed during sampling and thermal desorption analysis: Indicators of reactive species indoors. *Atmospheric Environment* 31, 715-725.
- Clausen PA, Wilkins CK, Wolkoff P, Nielsen GD, 2001. Chemical and biological evaluation of a reaction mixture of R-(+)-limonene/ozone — Formation of strong airway irritants. *Environment International* 26, 511-522.
- Cogliano VJ, Grosse Y, Baan RA, Straif K, Secretan MB, El Ghissassi F, 2005. Meeting report: Summary of IARC monographs on formaldehyde, 2-butoxyethanol, and 1-tert-butoxy-2-propanol. *Environmental Health Perspectives* 113, 1205-1208.
- Cohle SD, Thompson W, Eisenga BH, Cottingham SL, 2001. Unexpected death due to chloramine toxicity in a woman with a brain tumor. *Forensic Science International* 24, 137-139.
- Colombo A, De Bortoli M, Knoppel H, Schauenburg H, Vissers H, 1991. Small chamber tests and headspace analysis of volatile organic compounds emitted from household products. *Indoor Air* 1, 13-21.
- Colombo A, De Bortoli M, Knöppel H, Pecchio E, Visser H, 1993. Adsorption of selected volatile organic compounds on a carpet, a wall coating, and a gypsum board in a test house. *Indoor Air* 3, 276-282.
- Cooper SD, Raymer JH, Pellizzari ED, Thomas KW, 1995. The identification of polar organic compounds found in consumer products and their toxicological properties. *Journal of Exposure Analysis and Environmental Epidemiology* 5, 57-75.
- Corchnoy SB, Atkinson R, 1990. Kinetics of the gas-phase reactions of OH and NO₃ radicals with 2-carene, 1,8-cineole, p-cymene, and terpinolene. *Environmental Science & Technology* 24, 1497-1502.
- Cox SS, Zhao DY, Little JC, 2001. Measuring partition and diffusion coefficients for volatile organic compounds in vinyl flooring. *Atmospheric Environment* 35, 3823-3830.

- Devos M, Patte F, Rouault J, Laffort P, Van Gemert LJ, 1990. Standardized Human Olfactory Thresholds. Oxford University Press, New York.
- Docherty KS, Wu W, Lim YB, Ziemann PJ, 2005. Contributions of organic peroxides to secondary aerosol formed from reactions of monoterpenes with O₃, *Environmental Science & Technology* 39, 4049-4059.
- Drescher AC, Lobascio C, Gadgil AJ, Nazaroff WW, 1995. Mixing of a point-source indoor pollutant by forced convection. *Indoor Air* 5, 204-214.
- Dunn S, Ozere RL, 1966. Ammonia inhalation poisoning — Household variety. *Canadian Medical Association Journal* 94, 401.
- Elkilani A, Bouhamra W, Crittenden BD, 2001. An indoor air quality model that includes the sorption of VOCs on fabrics. *Process Safety and Environmental Protection* 79, 233-243.
- Elkilani AS, Baker CGJ, Al-Shammari QH, Bouhamra WS, 2003. Sorption of volatile organic compounds on typical carpet fibers. *Environment International* 29, 575-585.
- Ewers L, Clark S, Menrath W, Succop P, Bornschein R, 1994. Cleanup of lead in household carpet and floor dust. *American Industrial Hygiene Association Journal* 55, 650-657.
- Faigel HC, 1964. Hazards to health: Mixtures of household cleaning agents. *New England Journal of Medicine* 271, 618.
- Fan Z, Liou P, Weschler C, Fiedler N, Kipen H, Zhang J, 2003. Ozone-initiated reactions with mixtures of volatile organic compounds under simulated indoor conditions. *Environmental Science & Technology* 37, 1811-1821.
- Fan Z, Weschler CJ, Han I-K, Zhang J, 2005. Co-formation of hydroperoxides and ultra-fine particles during the reactions of ozone with a complex VOC mixture under simulated indoor conditions. *Atmospheric Environment* 39, 5171-5182.
- FFHPVC, 2001. Test Plan for Terpenoid Tertiary Alcohols and Related Esters. The Flavor and Fragrance High Production Volume Consortia, The Terpene Consortium, Washington DC. Submitted to the EPA under the HPV Challenge Program. Accessible at www.epa.gov/chemrtk/terpriar/c12965tp.pdf.
- Fick J, Pommer L, Andersson B, Nilsson C, 2001. Ozone removal in the sampling of parts per billion levels of terpenoid compounds: An evaluation of different scrubber materials. *Environmental Science & Technology* 35, 1458-1462.
- Fick J, Pommer L, Andersson B, Nilsson C, 2002. A study of the gas-phase ozonolysis of terpenes: The impact of radicals formed during the reaction. *Atmospheric Environment* 36, 3299-3308.
- Fick J, 2003. Chemical Reactions in Ventilation Systems: Ozonolysis of Monoterpenes. PhD Dissertation, Department of Chemistry, Umeå University, Umeå, Sweden.
- Fick J, Pommer L, Nilsson C, Andersson B, 2003. Effect of OH radicals, relative humidity, and time on the composition of the products formed in the ozonolysis of alpha-pinene. *Atmospheric Environment* 37, 4087-4096.
- Finlayson-Pitts BJ, Pitts Jr JN, 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, Orlando.
- Fortmann R, Ng A, Roache N, Howard E, 1999. Gas-phase and particulate emissions during application of a water-based cleaner with a hand pump sprayer. Proceedings of the 8th International Conference on Indoor Air Quality and Climate — Indoor Air '99, Edinburgh, Scotland, Vol. 3, pp 31-36.
- Franke DL, Cole EC, Leese KE, Foarde KK, Berry MA, 1997. Cleaning for improved indoor air quality: An initial assessment of effectiveness. *Indoor Air* 7, 41-54.

- Gapany-Gapanavicius M, Yellin A, Almog S, Tirosh M, 1982a. Pneumomediastinum: A complication from mixing household cleaning agents. *Journal of the American Medical Association* 248, 349-350.
- Gapany-Gapanavicius M, Molho M, Tirosh M, 1982b. Chloramine-induced pneumonitis from mixing household cleaning agents. *British Medical Journal* 285, 1086.
- Gibson WB, Keller PR, Foltz DJ, Harvey GJ, 1991. Diethylene glycol mono butyl ether concentrations in room air from application of cleaner formulations to hard surfaces. *Journal of Exposure Analysis and Environmental Epidemiology* 1, 369-383.
- Girman JR, Hodgson AT, Wind ML, 1987. Considerations in evaluating emissions from consumer products. *Atmospheric Environment* 21, 315-320.
- Glasius M, Lahaniati M, Calogirou A, Di Bella D, Jensen NR, Hjorth J, Kotzias D, Larsen BR, 2000. Carboxylic acids in secondary aerosols from oxidation of cyclic monoterpenes by ozone. *Environmental Science & Technology* 34, 1001-1010.
- Gong H, Matsunaga A, Ziemann PJ, 2005. Products and mechanism of secondary organic aerosol formation from reactions of linear alkenes with NO₃ radicals, *Journal of Physical Chemistry A* 109, 4312-4324.
- Gosselin RE, Smith RP, Hodge HC, 1984. *Clinical Toxicology of Commercial Products*. Williams & Wilkins, Baltimore.
- Greene CR, Atkinson R, 1992. Rate constants for the gas-phase reactions of O₃ with a series of alkenes at 296 ± 2 K, *International Journal of Chemical Kinetics* 24, 803-811.
- Griffin RJ, Cocker III DR, Flagan RC, Seinfeld JH, 1999. Organic aerosol formation from the oxidation of biogenic hydrocarbons. *Journal of Geophysical Research* 104, 3555-3567.
- Grøntoft T, Henriksen JF, Seip HM, 2004. The humidity dependence of ozone deposition onto a variety of building surfaces. *Atmospheric Environment* 38, 59-68.
- Grosjean D, Williams II EL, 1992. Environmental persistence of organic compounds estimated from structure-reactivity and linear free-energy relationships. Unsaturated aliphatics. *Atmospheric Environment* 26A, 1395-1405.
- Grosjean D, Williams EL, Grosjean E, Andino JM, Seinfeld JH, 1993. Atmospheric oxidation of biogenic hydrocarbons — Reaction of ozone with beta-pinene, d-limonene and trans-caryophyllene. *Environmental Science & Technology* 27, 2754-2758.
- Gupta P, Harger WP, Arey J, 1996. The contribution of nitro- and methyl-nitro-naphthalenes to the vapor-phase mutagenicity of ambient air samples. *Atmospheric Environment* 30, 3157-3166.
- Haghighat F, Megri AC, 1996. A comprehensive validation of two airflow models — COMIS and CONTAM. *Indoor Air* 6, 278-288.
- Hallquist M, Wangberg I, Ljungstrom E, 1997. Atmospheric fate of carbonyl oxidation products originating from alpha-pinene and delta(3)-carene: Determination of rate of reaction with OH and NO₃ radicals, UV absorption cross sections, and vapor pressures. *Environmental Science & Technology* 31, 3166-3172.
- Ham JE, Proper SP, Wells JR, 2006. Gas-phase chemistry of citronellol with ozone and OH radical: Rate constants and products. *Atmospheric Environment* 40, 726-735.
- Hand JL, Kreidenweis SM, 2001. A new technique for obtaining aerosol size distributions with applications to estimates of aerosol properties. CIRA Technical Paper No. 0737-5352-49, Colorado State University, Fort Collins, CO.

- Hatakeyama S, Izumi K, Fukuyama T, Akimoto H, 1989. Reactions of ozone with alpha-pinene and beta-pinene in air — Yields of gaseous and particulate products. *Journal of Geophysical Research — Atmospheres* 94, 13013-13024.
- Hattis RP, Greer JR, Dietrich S, Olafsson S, McAndrew KR, 1991. Chlorine gas toxicity from mixture of bleach with other cleaning products — California. *Morbidity and Mortality Weekly Report* 40, 619-629 & 646.
- Hegarty JM, Rouhbakhsh S, Warner JA, Warner JO, 1995. A comparison of the effect of conventional and filter vacuum cleaners on airborne house-dust mite allergen. *Respiratory Medicine* 89, 279-284.
- Henneberger PK, Derk SJ, Davis L, Tumpowsky C, Reilly MJ, Rosenman KD, Schill DP, Valiante D, Flattery J, Harrison R, Reinisch F, Filios MS, Tift B, 2003. Work-related reactive airways dysfunction syndrome cases from surveillance in selected US states. *Journal of Occupational and Environmental Medicine* 45, 360-368.
- Hodgson AT, Rudd AF, Beal D, Chandra S, 2000. Volatile organic compound concentrations and emission rates in new manufactured and site-built houses. *Indoor Air* 10, 178-192.
- Hodgson AT, Levin H, 2003. Volatile organic compounds in indoor air: A review of concentrations measured in North America since 1990. Report LBNL-51715, Lawrence Berkeley National Laboratory, Berkeley, CA.
- Hoffmann T, Odum JR, Bowman F, Collins D, Klockow D, Flagan RC, Seinfeld JH, 1997. Formation of organic aerosols from the oxidation of biogenic hydrocarbons. *Journal of Atmospheric Chemistry* 26, 189-222.
- Howard PH, Meylan WM. *Handbook of Physical Properties of Organic Chemicals*. Boca Raton, FL: CRC-Lewis Publishers, 1997.
- Howard-Reed C, Wallace LA, Ott WR, 2002. The effect of opening windows on air change rates in two homes. *Journal of the Air & Waste Management Association* 52, 147-159.
- Hubbard HF, Coleman BK, Sarwar G, Corsi RL, 2005. The effects of an ozone generating air purifier on indoor secondary particles in three residential dwellings. *Indoor Air* 15, 432-444.
- Jaakkola JJK, Piipari R, Jaakkola MS, 2003. Occupation and asthma: A population-based incident case-control study. *American Journal of Epidemiology* 158, 981-987.
- Jang M, Kamens RM, 1999. Newly characterized products and composition of secondary aerosols from the reaction of α -pinene and ozone. *Atmospheric Environment* 33, 459-474.
- Jenkins PL, Phillips TJ, Mulberg EJ, Hui SP, 1992. Activity patterns of Californians: Use of and proximity to indoor pollutant sources. *Atmospheric Environment* 26A, 2141-2148.
- Jerrim KL, Hughes JF, McKechnie MT, 2001. Electrostatic enhancement of dust and allergen removal from carpets. *Journal of Electrostatics* 53, 39-51.
- Jerrim KL, Whitmore LF, Hughes JF, McKechnie MT, 2002. Airborne dust and allergen generation during dusting with and without spray polish. *Journal of Allergy and Clinical Immunology* 109, 63-67.
- Jones FL, 1972. Chlorine poisoning from mixing household cleaners. *Journal of the American Medical Association* 222, 1312.
- Jørgensen RB, Bjørseth O, 1999. Sorption behaviour of volatile organic compounds on material surfaces — The influence of combinations of compounds and materials compared to sorption of single compounds on single materials. *Environment International* 25, 17-27.
- Jørgensen RB, Bjørseth O, Malvik B, 1999. Chamber testing of adsorption of volatile organic compounds (VOCs) on material surfaces. *Indoor Air* 9, 2-9.

- Jørgensen RB, Dokka TH, Bjørseth O, 2000. Introduction of a sink-diffusion model to describe the interaction between volatile organic compounds (VOCs) and material surfaces. *Indoor Air* 10, 27-38.
- Josephson KL, Rubino JR, Pepper IL, 1997. Characterization and quantification of bacterial pathogens and indicator organisms in household kitchens with and without the use of a disinfectant cleaner. *Journal of Applied Microbiology*, 83, 737-750.
- Karjalainen A, Martikainen R, Karjalainen J, Klaukka T, Kurppa K, 2002. Excess incidence of asthma among Finnish cleaners employed in different industries. *European Respiratory Journal* 19, 90-95.
- Karlberg AT, Magnusson K, Nilsson U, 1992. Air oxidation of d-limonene (the citrus solvent) creates potent allergens. *Contact Dermatitis* 26, 332-340.
- Karlberg AT, Shao LP, Nilsson U, Gafvert E, Nilsson JLG, 1994. Hydroperoxides in oxidized d-limonene identified as potent contact allergens. *Archives of Dermatological Research* 286, 97-103.
- Kavouras IG, Mihalopolous N, Stephanou EG, 1998. Formation of atmospheric particles from organic acids produced by forests. *Nature* 395, 683-686.
- Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Wiley, New York, 1998.
- Klenø J, Wolkoff P, 2004. Changes in eye blink frequency as a measure of trigeminal stimulation by exposure to limonene oxidation products, isoprene oxidation products and nitrate radicals. *International Archives of Occupational and Environmental Health* 77, 235-243.
- Klenø-Nojgaard J, Christensen KB, Wolkoff P, 2005. The effect on human eye blink frequency of exposure to limonene oxidation products and methacrolein. *Toxicology Letters* 156, 241-251.
- Knöppel H, Schauenburg H, 1989. Screening of household products for the emission of volatile organic compounds. *Environment International* 15, 413-418.
- Kogevinas M, Antó JM, Sunyer J, Tobias A, Kromhout H, Burney P, and the European Community Respiratory Health Survey Study Group, 1999. Occupational asthma in Europe and other industrialized areas: A population based study. *Lancet* 353, 1750-1754.
- Kovacs DC, Small MJ, Davidson CI, Fischhoff B, 1997. Behavioral factors affecting exposure potential for household cleaning products. *Journal of Exposure Analysis and Environmental Epidemiology* 7, 505-520.
- Kreiss K, Gonzalez MG, Conright KL, Scheere AR, 1982. Respiratory irritation due to carpet shampoo: Two outbreaks. *Environment International* 8, 337-341.
- Kroll JH, Donahue NM, Cee VJ, Demerjian KL, Anderson JG, 2002. Gas-phase ozonolysis of alkenes: Formation of OH from anti carbonyl oxides. *Journal of the American Chemical Society* 124, 8518-8519.
- Kulmala M, Vehkamäki H, Petäjä T, Dal Maso M, Lauri A, Kerminen VM, Birmili W, McMurry PH, 2004. Formation and growth rates of ultrafine atmospheric particles: A review of observations. *Journal of Aerosol Science* 35, 143-176.
- Lai ACK, Thatcher TL, Nazaroff WW, 2000. Inhalation transfer factors for air pollution health-risk assessments, *Journal of the Air & Waste Management Association* 50, 1688-1699.
- Laumbach RJ, Fiedler N, Gardner CR, Laskin DL, Fan Z, Zhang J, Weschler CJ, Liou PJ, Devlin RB, Ohman-Strickland P, Kelly-McNeil K, and Kipen HM, 2005. Nasal effects of a mixture of volatile organic compounds and their ozone oxidation products. *Journal of Environmental and Occupational Medicine* 47 (in press).

- Lee K, Vallarino J, Dumyahn T, Ozkaynak H, Spengler JD, 1999. Ozone decay rates in residences. *Journal of the Air & Waste Management Association* 49, 1238-1244.
- Lee SC, Lam S, Fai HK, 2001. Characterization of VOCs, ozone, and PM₁₀ emissions from office equipment in an environmental chamber. *Building and Environment* 36, 837-842.
- Leovic KW, Sheldon LS, Whitaker DA, Hetes RG, Calcagni JA, Baskir JN, 1996. Measurement of indoor air emissions from dry-process photocopy machines. *Journal of the Air & Waste Management Association* 46, 821-829.
- Leungsakul S, Jaoui M, Kamens RM, 2005. Kinetic mechanisms for predicting secondary organic aerosol formation from the reaction of d-limonene with ozone. *Environmental Science & Technology* 39 (in press) doi:10.1021/es0492687.
- Li TH, 2001. Generation, Characterization, Aerosol Partitioning, and Indoor Measurements of Hydrogen Peroxide for Exposure and Toxicological Assessment. PhD Dissertation, Graduate Program in Environmental Science and Public Health, Graduate School New Brunswick of Rutgers.
- Li TH, Turpin BJ, Shields HC, Weschler CJ, 2002. Indoor hydrogen peroxide derived from ozone/d-limonene reactions. *Environmental Science & Technology* 36, 3295-3302.
- Lioy PJ, Yiin LM, Adgate J, Weisel C, Rhoads GG, 1998. The effectiveness of a home cleaning intervention strategy in reducing potential dust and lead exposures. *Journal of Exposure Analysis and Environmental Epidemiology* 8, 17-35.
- Liu XY, Mason M, Krebs K, Sparks L, 2004. Full-scale chamber investigation and simulation of air freshener emissions in the presence of ozone. *Environmental Science & Technology* 38, 2802-2812.
- Long CM, Suh HH, Koutrakis P, 2000. Characterization of indoor particle sources using continuous mass and size monitors. *Journal of the Air & Waste Management Association* 50, 1236-1250.
- Lynch RM, 2000. Modeling of exposure to carpet-cleaning chemicals preceding irritant-induced asthma in one patient, *Environmental Health Perspectives* 108, 911-913.
- Maroni M, Seifert B, Lindvall T, 1995. *Indoor Air Quality — A Comprehensive Reference Book*. Elsevier, Amsterdam.
- Marty MA, Blaisdell RJ, Broadwin R, Hill M, Shimer D, Jenkins M, 2002. Distribution of daily breathing rates for use in California's Air Toxics Hot Spots Program risk assessments. *Human and Ecological Risk Assessment* 8, 1723-1737.
- Matthews TG, Hawthorne AR, Thompson CV, 1987. Formaldehyde sorption and desorption characteristics of gypsum wallboard. *Environmental Science & Technology* 21, 629-634.
- Medina-Ramón M, Zock JP, Kogevinas M, Sunyer J, Antó JM, 2003. Asthma symptoms in women employed in domestic cleaning: A community based study. *Thorax* 58, 950-954.
- Medina-Ramón M, Zock JP, Kogevinas M, Sunyer J, Torralba Y, Borrell A, Burgos F, Antó JM, 2005. Asthma, chronic bronchitis, and exposure to irritant agents in occupational domestic cleaning: A nested case-control study. *Occupational and Environmental Medicine* 62, 598-606.
- Meininghaus R, Salthammer T, Knoppel H, 1999. Interaction of volatile organic compounds with indoor materials — A small-scale screening method. *Atmospheric Environment* 33, 2395-2401.
- Meininghaus R, Kirchner S, Maupetit F, Sallee H, Quenard D, 2000. Gravimetric studies on VOC adsorption by indoor materials under near-ambient conditions. *Indoor + Built Environment* 9, 277-283.

- Meininghaus R, Uhde E, 2002. Diffusion studies of VOC mixtures in a building material. *Indoor Air* 12, 215-222.
- Mendonça EMC, Algranti E, de Freitas JBP, Rosa EA, Freire JAD, Santos UD, Pinto J, Bussacos MA, 2003. Occupational asthma in the city of Sao Paulo, 1995-2000, with special reference to gender analysis. *American Journal of Industrial Medicine* 43, 611-617.
- Mølhave L, Kjaergaard SK, Hempel-Jørgensen A, Juto JE, Andersson K, Stridh G, Falk J, 2000. The eye irritation and odor potencies of four terpenes which are major constituents of the emissions of VOCs from Nordic soft woods. *Indoor Air* 10, 315-318.
- Morrison GC, 1999. Ozone-Surface Interactions: Investigation of Mechanisms, Kinetics, Mass Transport, and Implications for Indoor Air Quality. PhD Dissertation, Civil and Environmental Engineering Department, University of California, Berkeley.
- Mrvos R, Dean BS, Krenzelok EP, 1993. Home exposures to chlorine chloramine gas — Review of 216 cases. *Southern Medical Journal* 86, 654-657.
- Murphy DMF, Fairman RP, Lapp NL, Morgan WKC, 1976. Severe airway disease due to inhalation of fumes from cleansing agents. *Chest* 69, 372-376.
- Murray DM, Burmaster DE, 1995. Residential air exchange rates in the United States: Empirical and estimated parametric distributions by season and climatic region. *Risk Analysis* 15, 459-465.
- Nazaroff WW, Cass GR, 1986. Mathematical modeling of chemically reactive pollutants in indoor air. *Environmental Science & Technology* 20, 924-934.
- Nazaroff WW, Singer BC, 2004. Inhalation of hazardous air pollutants from environmental tobacco smoke in US residences. *Journal of Exposure Analysis and Environmental Epidemiology* 14, S71-S77.
- Nielsen J, Bach E, 1999. Work-related eye symptoms and respiratory symptoms in female cleaners. *Occupational Medicine* 49, 291-297.
- NIH, 2004. Household Products Database. National Institutes of Health, Department of Health & Human Services, Specialized Information Services, U.S. National Library of Medicine, Bethesda, MD. Last update May 12, 2004.
- Nilsen SK, Dahl I, Jorgensen O, Schneider T, 2002. Micro-fiber and ultra-micro-fiber cloths, their physical characteristics, cleaning effect, abrasion on surfaces, friction, and wear resistance. *Building and Environment* 37, 1373-1378.
- Nilsson U, Bergh M, Shao LP, Karlberg AT, 1996. Analysis of contact allergenic compounds in oxidized d-limonene. *Chromatographia* 42, 199-205.
- NIST, 2000. National Institute of Standards and Technology. Chemical Kinetics Database. Standard Reference Database 17, Version 7.0, Release 1.3.
- Niu JL, Tung TCW, Burnett J, 2001. Ozone emission rate testing and ranking method using environmental chamber. *Atmospheric Environment* 35, 2143-2151.
- Nunes FMN, Veloso MCC, Pereira PA de P, de Andrade JB, 2005. Gas-phase ozonolysis of the monoterpenoids (*S*)-(+)-carvone, (*R*)-(—)-carvone, (-)-carveol, geraniol and citral. *Atmospheric Environment* 39, 7715-7730.
- OEHHA, 1999. Determination of acute reference exposure levels for airborne toxicants. Air Toxicology and Epidemiology Section, California Office of Environmental Health Hazard Assessment, March, 1999. (http://www.oehha.ca.gov/air/acute_rels/allAcRELS.html).
- OEHHA, 2000. Office of Environmental Health Hazard Assessment. Air Toxics Hot Spot Program Risk Assessment Guidelines. http://www.oehha.org/air/chronic_rels/

- OEHHA, 2003. Proposition 65 Status Report Safe Harbor Levels: No Significant Risk Levels for Carcinogens and Maximum Allowable Dose Levels for Chemicals Causing Reproductive Toxicity. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Sacramento, CA. Accessed at <http://www.oehha.ca.gov/prop65/pdf/June2003StatusReport.pdf>.
- OEHHA, 2005. Proposition 65 safe harbor levels: No significant risk levels for carcinogens and maximum allowable dose levels for chemicals causing reproductive toxicity. Reproductive and Cancer Hazard Assessment Branch, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, Sacramento.
- Olson W, Vesley D, Bode M, Dubbel P, Bauer T, 1994. Hard surface cleaning performance of six alternative household cleaners under laboratory conditions. *Journal of Environmental Health* 56, 27-31.
- Orlando JJ, Tyndall GS, Ceazan N, 2001. Rate coefficients and product yields from reaction of OH with 1-penten-3-ol, (Z)-2-penten-1-ol, and allyl alcohol (2-propen-1-ol). *Journal of Physical Chemistry A*, 105, 3564-3569
- Pascuzzi TA, Storrow AB, 1998. Mass casualties from acute inhalation of chloramine gas. *Military Medicine* 163(2), 102-104.
- Persily A, 1989. Ventilation rates in office buildings. IAQ '89 The Human Equation: Health and Comfort, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc., Atlanta, pp. 128-136.
- Phillips TJ, Bloudoff DP, Jenkins PL, Stroud KR, 1999. Ozone emissions from a "personal air purifier". *Journal of Exposure Analysis and Environmental Epidemiology* 9, 594-601.
- Pollmann J, Ortega J, Helmig D, 2005. Analysis of atmospheric sesquiterpenes: Sampling losses and mitigation of ozone interferences. *Environmental Science & Technology* 39, 9620-9629.
- Pommer L, 2003. Oxidation of Terpenes in Indoor Environments: A Study of Influencing Factors. PhD Dissertation, Department of Chemistry, Umeå University, Umeå, Sweden.
- Popa J, Haghighat F, 2003. The impact of VOC mixture, film thickness and substrate on adsorption/desorption characteristics of some building materials. *Building and Environment* 38, 959-964.
- Pope CA, Burnett RT, Thun MJ, Calle EE, Krewski D, Ito K, Thurston GD, 2002. Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. *Journal of the American Medical Association* 287, 1132-1141.
- Purohit A, Kopferschmitt-Kubler MC, Moreau C, Popin E, Blaumeiser M, Pauli G, 2000. Quaternary ammonium compounds and occupational asthma. *International Archives of Occupational and Environmental Health* 73(6), 423-427.
- Reisen F, Aschmann SM, Atkinson R, Arey J, 2003. Hydroxylaldehyde products from hydroxyl radical reactions of Z-3-hexen-1-ol and 2-methyl-3-buten-2-ol quantified by SPME and API-MS. *Environmental Science & Technology* 37, 4664-4671.
- Reisz GR, Gammon RS, 1986. Toxic pneumonitis from mixing household cleaners. *Chest* 89, 49-52.
- Roache N, Fortmann R, Ng A, Howard E, 2000. Characterization of aerosols from a water-based cleaner applied with a hand-pump sprayer. *Proceedings of Engineering Solutions to Indoor Air Quality Problems*, Air & Waste Management Association, July 17-19, pp 356-365.
- Robinson P, Tauxe R, Winkler W, Levy M, 1983. Respiratory illness in conference participants following exposure to rug shampoo. *Infection Control* 4, 158-160.

- Rogers JD, 1989. Rate constant measurements for the reaction of the hydroxyl radical with cyclohexene, cyclopentene, and glutaraldehyde. *Environmental Science & Technology* 23, 177-181.
- Rogers RE, Isola DA, Jeng C-J, Lefebvre A, Smith LW, 2005. Simulated inhalation of fragrance materials in a surrogate air freshener formulation. *Environmental Science & Technology* 39, 7810-7816.
- Rohr AC, Weschler CJ, Koutrakis P, Spengler JD, 2003. Generation and quantification of ultrafine particles through terpene/ozone reactions in a chamber setting. *Aerosol Science & Technology* 37, 65-78.
- Rosenman KD, Reilly MJ, Schill DP, Valiante D, Flattery J, Harrison R, Reinisch F, Pechter E, Davis L, Tumpowsky CM, Filios M, 2003. Cleaning products and work-related asthma. *Journal of Occupational and Environmental Medicine* 45, 556-563.
- Rudel RA, Camann DE, Spengler JD, Korn LR, Brody JG, 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor air and dust. *Environmental Science & Technology* 37, 4543-4553.
- Rusin P, Orosz-Coughlin P, Gerba C, 1998. Reduction of faecal coliform, coliform and heterotrophic plate count bacteria in the household kitchen and bathroom by disinfection with hypochlorite cleaners. *Journal of Applied Microbiology* 85, 819-828.
- Sack TM, Steele DH, Hammerstrom K, Remmers J, 1992. A survey of household products for volatile organic compounds. *Atmospheric Environment* 26, 1063-1070.
- Salthammer T, 1999. Volatile organic ingredients of household and consumer products. In: Salthammer T (Ed.), *Organic Indoor Air Pollutants*, Wiley-VCH, Weinheim, pp. 219-232.
- Sarwar G, Corsi R, Allen D, Weschler CJ, 2002a. Production and levels of selected indoor radicals: A modeling assessment. In *Indoor Air 2002: Proceedings of the 9th International Conference on Indoor Air Quality and Climate*, Vol. 5, Levin H (Ed.), Indoor Air 2002, Santa Cruz, California, pp. 80-85.
- Sarwar G, Corsi R, Kimura Y, Allen D, Weschler CJ, 2002b. Hydroxyl radicals in indoor environments. *Atmospheric Environment* 36, 3973-3988.
- Sarwar G, Corsi R, Allen D, Weschler CJ, 2003. The significance of secondary organic aerosol formation and growth in buildings: Experimental and computational evidence. *Atmospheric Environment* 37, 1365-1381.
- Sarwar G, Olson DA, Corsi RL, Weschler CJ, 2004. Indoor fine particles: The role of terpene emissions from consumer products. *Journal of the Air & Waste Management Association* 54, 367-377.
- Savonius B, Keskinen H, Tuppurainen M, Kanerva L, 1994. Occupational asthma caused by ethanalamines. *Allergy* 49, 877-881.
- Schneider T, Lobner T, Nilsen SK, Petersen OH, 1994. Quality of cleaning quantified. *Building and Environment* 29, 363-367.
- Sherriff A, Farrow A, Golding J, the ALSPAC Study Team, Henderson J, 2005. Frequent use of chemical household products is associated with persistent wheezing in pre-school age children. *Thorax* 60, 45-49.
- Shepherd JL, Corsi RL, Kemp J, 1996. Chloroform in indoor air and wastewater: The role of residential washing machines. *Journal of the Air & Waste Management Association* 46, 631-642.

- Shorees B, Atkinson R, Arey J, 1991. Kinetics of the gas-phase reactions of β -phellandrene with OH and NO₃ radicals and O₃ at 297 \pm 2 K, *International Journal of Chemical Kinetics* 23, 897-906.
- Shu Y, Atkinson R, 1994. Rate constants for the gas-phase reactions of O₃ with a series of terpenes and OH radical formation from the O₃ reactions with sesquiterpenes at 296 \pm 2 K. *International Journal of Chemical Kinetics* 26, 1193-1205.
- Shu Y, Atkinson R, 1995. Atmospheric lifetimes and fates of a series of sesquiterpenes. *Journal of Geophysical Research* 100, 7275-7281.
- Shu Y, Kwok ESC, Tuazon EC, Atkinson R, Arey J, 1997. Products of the gas-phase reactions of linalool with OH radicals, NO₃ radicals and O₃. *Environmental Science & Technology* 31, 896-904.
- Siese M, Becker KH, Brockmann KJ, Geiger H, Hofzumahaus A, Holland F, Mihelcic D, Wirtz K, 2001. Direct measurement of OH radicals from ozonolysis of selected alkenes: a EUPHORE simulation chamber study. *Environmental Science & Technology* 35, 4660-4667.
- Singer BC, Hodgson AT, Guevarra KS, Hawley EL, Nazaroff WW, 2002. Gas-phase organics in environmental tobacco smoke: 1. Effects of smoking rate, ventilation, and furnishing level on emission factors. *Environmental Science & Technology* 36, 846-853.
- Singer BC, Revzan KL, Hotchi T, Hodgson AT, Brown NJ, 2004. Sorption of organic gases in a furnished room. *Atmospheric Environment* 38, 2483-2494.
- Singer BC, Hodgson AT, Hotchi T, Ming KY, Sextro RG, Wood EE, Brown NJ, 2005. Sorption of organic gases in residential bedrooms and bathrooms. *Proceedings of Indoor Air 2005, The 10th International Conference on Indoor Air Quality and Climate, Beijing, China*. Also available as report LBNL-56787, Lawrence Berkeley National Laboratory, Berkeley, CA.
- Skold M, Borje A, Matura M, Karlberg AT, 2002. Studies on the autoxidation and sensitizing capacity of the fragrance chemical linalool, identifying a linalool hydroperoxide. *Contact Dermatitis* 46, 267-272.
- Smith KR, 1988. Air pollution: Assessing total exposure in the United States. *Environment* 30 (8), 10-15, 33-38, October.
- Smith KR, 2002. Place makes the poison: Wesolowski Award Lecture — 1999. *Journal of Exposure Analysis and Environmental Epidemiology* 12, 167-171.
- Sorensen DN, Weschler CJ, 2002. Modeling gas phase reactions in indoor environments using computational fluid dynamics. *Atmospheric Environment* 36, 9-18.
- Sparks LE, Tichenor BA, White JB, Jackson MD, 1991. Comparison of data from an IAQ test house with predictions of an IAQ computer model. *Indoor Air* 1, 577-592.
- Sparks LE, Guo Z, Chang JC, Tichenor BA, 1999. Volatile organic compound emissions from latex paint — Part 1. Chamber experiments and source model development. *Indoor Air* 9, 10-17.
- Spaulding RS, Schade GW, Goldstein AH, Charles MJ, 2003. Characterization of secondary atmospheric photooxidation products: Evidence for biogenic and anthropogenic sources. *Journal of Geophysical Research - Atmospheres* 108(D8), art. 4247.
- Steiber RS, 1995. Increases in levels of breathable fine particulates due to the application of carpet fresheners in a suburban home, in *Engineering Solutions to Indoor Air Quality Problems*, Air & Waste Management Association, Research Triangle Park, NC, 24-26 July 1995, pp. 29-38.

- Stemmler K, Kinnison DJ, Kerr JA, 1996. Room temperature rate coefficients for the reactions of OH radicals with some monoethylene glycol monoalkyl ethers. *Journal of Physical Chemistry* 100, 2114-2116.
- Stemmler K, Mengon W, Kinnison DJ, Kerr JA, 1997. OH radical-initiated oxidation of 2-butoxyethanol under laboratory conditions related to the troposphere: Product studies and proposed mechanism. *Environmental Science & Technology* 31, 1496-1504.
- Tamás G, Weschler CJ, Tøftum J, Fanger PO, 2005. Influence of ozone-limonene reactions on perceived air quality. *Indoor Air* 15 (in press).
- Tanen DA, Graeme KA, Raschke R, 1999. Severe lung injury after exposure to chloramine gas from household cleaners. *New England Journal of Medicine* 341, 848-849.
- Ten Brinke J, Selvin S, Hodgson AT, Fisk WJ, Mendell MJ, Koshland CP, Daisey JM, 1998. Development of new volatile organic compound (VOC) exposure metrics and their relationship to sick building syndrome symptoms. *Indoor Air* 8, 140-152.
- Tichenor BA, Mason MA, 1988. Organic emissions from consumer products and building materials to the indoor environment. *JAPCA — The International Journal of Air Pollution Control and Hazardous Waste Management* 38, 264-268.
- Tichenor BA, Guo Z, Dunn JE, Sparks LE, Mason MA, 1991. The interaction of vapour phase organic compounds with indoor sinks. *Indoor Air* 1, 23-35.
- Tobias HJ, Docherty KS, Beving DE, Ziemann PJ, 2000. Effect of relative humidity on the chemical composition of secondary organic aerosol formed from reactions of 1-tetradecene and O₃. *Environmental Science & Technology* 34, 2116-2125.
- Tobias HJ, Ziemann PJ, 2000. Thermal desorption mass spectrometric analysis of organic aerosol formed from reactions of 1-tetradecene and O₃ in the presence of alcohols and carboxylic acids. *Environmental Science & Technology* 34, 2105-2115.
- Tuazon EC, Arey J, Atkinson R, Aschmann SM, 1993. Gas-phase reactions of 2-vinylpyridine and styrene with OH and NO₃ radicals and O₃. *Environmental Science & Technology* 27, 1832-1841.
- Turpin BJ, Lim HJ, 2001. Species contribution to PM_{2.5} mass concentrations: Revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602-610.
- US Department of Labor, 2001. National occupational employment and wage estimates: Building and grounds cleaning and maintenance occupations. Accessed at http://www.bls.gov/oes/2001/oes_37Bu.htm.
- USEPA, 1984. Method TO-1, Revision 1.0: Method for the Determination of Volatile Organic Compounds in Ambient Air Using Tenax® Adsorption and Gas Chromatography/Mass Spectrometry (GC/MS). Center for Environmental Research Information, Office of Research and Development, United States Environmental Protection Agency.
- USEPA, 2003. List of hazardous air pollutants, petition process, lesser quantity designations, source category list. *Federal Register* 68 (225), 65648-65663, 21 November 2003.
- USEPA, 2004a. List of hazardous air pollutants, petition process, lesser quantity designations, source category list; petition to delist of ethylene glycol monobutyl ether. *Federal Register* 69 (228), 69320-69325, 29 November 2004.
- USEPA, 2004b. The ozone report — Measuring progress through 2003. Report No. EPA 454/K-04-001, US Environmental Protection Agency. <http://www.epa.gov/airtrends/ozone.html>.
- Van der Wal JF, Hoogeveen AK, van Leeuwen L, 1998. A quick screening method for sorption effects of volatile organic compounds on indoor materials. *Indoor Air* 8, 103-112.

- VanOsdell DW, Owen MK, Jaffe LB, Sparks LE, 1996. VOC removal at low contaminant concentrations using granular activated carbon. *Journal of the Air & Waste Management Association* 46, 883-890.
- Vaughan JW, Woodfolk JA, Platts-Mills TAE, 1999. Assessment of vacuum cleaners and vacuum cleaner bags recommended for allergic subjects. *Journal of Allergy and Clinical Immunology* 104, 1079-1083.
- Vejrup KV, Wolkoff P, 1994. VOC emissions from some floor-cleaning agents, in *Healthy Buildings '94*, Banhidi L, Farkas I, Magyar Z, Rudnai P (eds), *Healthy Buildings '94*, Budapest, Hungary, pp. 247-252.
- Vejrup KV, 1996. The Importance of Chemical Components in Cleaning Agents for the Indoor Environment. PhD Thesis. National Institute of Occupational Health and Danish Technical University, Copenhagen, Denmark. As cited in Wolkoff et al., 1998.
- Vejrup KV, Wolkoff P, 2002. Linear alkylbenzene sulfonates in indoor floor dust. *The Science of the Total Environment* 300, 51-58.
- Virkkula A, Van Dingenen R, Raes F, Hjorth J, 1999. Hygroscopic properties of aerosol formed by oxidation of limonene, alpha-pinene and beta-pinene. *Journal of Geophysical Research* 104, 3569-3579.
- Wainman T, Zhang JF, Weschler CJ, Liou PJ, 2000. Ozone and limonene in indoor air: A source of submicron particle exposure. *Environmental Health Perspectives* 108, 1139-1145.
- Wallace LA, Pellizzari E, Leaderer B, Zelon H, Sheldon L, 1987. Emissions of volatile organic compounds from building materials and consumer products. *Atmospheric Environment*, 21, 385-393.
- Webb AM, Singer BC, Nazaroff WW, 2002. Effect of gaseous ammonia on nicotine sorption. In *Indoor Air 2002: Proceedings of the 9th International Conference on Indoor Air Quality and Climate*, Vol. 3, Levin H (ed.), Indoor Air 2002, Santa Cruz, CA, pp. 512-517.
- Weegels MF, van Veen MP, 2001. Variation of consumer contact with household products: A preliminary investigation. *Risk Analysis* 21, 499-511.
- Wells JR, 2005. Gas-phase chemistry of α -terpineol with ozone and OH radical: Rate constants and products. *Environ. Sci. Technol.* 39, 6937-6943
- Weschler CJ, Brauer M, Koutrakis P, 1992. Indoor ozone and nitrogen dioxide: A potential pathway to the generation of nitrate radical, dinitrogen pentoxide and nitric acid indoors. *Environmental Science & Technology* 26, 179-184.
- Weschler CJ, Shields HC, Naik DV, 1994. Indoor chemistry involving O₃, NO and NO₂ as evidenced by 14 months of measurements at a site in Southern California. *Environmental Science & Technology* 28, 2120-2132.
- Weschler CJ, Shields HC, 1996. Production of hydroxyl radical in indoor air. *Environmental Science & Technology* 30, 3250-3258.
- Weschler CJ, Shields HC, 1997a. Measurements of the hydroxyl radical in a manipulated but realistic indoor environment. *Environmental Science & Technology* 31, 3719-3722.
- Weschler CJ, Shields HC, 1997b. Potential reactions among indoor pollutants. *Atmospheric Environment* 31, 3487-3495.
- Weschler CJ, Shields HC, 1999. Indoor ozone/terpene reactions as a source of indoor particles. *Atmospheric Environment* 33, 2301-2312.
- Weschler CJ, Shields HC, 2000. The influence of ventilation on reactions among indoor pollutants: Modeling and experimental observations. *Indoor Air* 10, 92-100.

- Weschler CJ, 2000. Ozone in indoor environments: Concentration and chemistry. *Indoor Air* 10, 269-288.
- Weschler CJ, 2001. Reactions among indoor pollutants. *The Scientific World* 1, 443-457.
- Weschler CJ, 2003a. Indoor chemistry as a source of particles. In: Morawska L, Salthammer T (Ed.) *Indoor Environment: Airborne Particles and Settled Dust*, Wiley-VCH, Weinheim, pp. 171-194.
- Weschler CJ, 2003b. Indoor/outdoor connections exemplified by processes that depend on an organic compound's saturation vapor pressure. *Atmospheric Environment* 37, 5455-5465.
- Weschler CJ, Shields HC, 2003. Experiments probing the influence of air exchange rates on secondary organic aerosols derived from indoor chemistry. *Atmospheric Environment* 37, 5621-5631.
- Weschler CJ, 2004a. Ozone-initiated reaction products indoors may be more harmful than ozone itself. *Atmospheric Environment* 38, 5715-5716.
- Weschler CJ, 2004b. Chemical reactions among indoor pollutants: What we've learned in the new millennium. *Indoor Air* 14 (Supplement 7), 184-194.
- Weschler CJ, Wells JR, Poppendieck D, Hubbard H, Pearce TA, 2005. Indoor chemistry and health — A workshop summary. *Environmental Health Perspectives* 114 (in press) doi:10.1289/ehp.8271.
- Wiley JA, Robinson JP, Piazza T, Garrett K, Cirksena K, Cheng YT, Martin G, 1991. Activity patterns of California residents. Final Report Contract No. A6-177-33. California Air Resources Board, Sacramento, CA.
- Wilson AL, Colome SD, Tian Y, Becker EW, Baker PE, Behrens DW, Billick IH, Garrison CA, 1996. California residential air exchange rates and residence volumes. *Journal of Exposure Analysis and Environmental Epidemiology* 6, 311-326.
- Wolkoff P, Clausen PA, Nielsen PA, 1995. Application of field and laboratory emission cell 'FLEC' — Performance study, intercomparison study, and case study of damaged linoleum. *Indoor Air* 5, 196-203.
- Wolkoff P, Clausen PA, Jensen B, Nielsen GD, Wilkins CK, 1997. Are we measuring the relevant indoor pollutants? *Indoor Air* 7, 92-106.
- Wolkoff P, Schneider T, Kildesø J, Degerth R, Jaroszewski M, Schunk H, 1998. Risk in cleaning: Chemical and physical exposure. *The Science of the Total Environment* 215, 135-156.
- Wolkoff P, Clausen PA, Wilkins CK, Nielsen GD, 2000. Formation of strong airway irritants in terpene/ozone mixtures. *Indoor Air* 10, 82-91.
- Wolkoff P, Nielsen GD, 2001. Organic compounds in indoor air – their relevance for perceived indoor air quality? *Atmospheric Environment* 35, 4407-4417.
- Won D, Corsi RL, Rynes M, 2000. New indoor carpet as an adsorptive reservoir for volatile organic compounds. *Environmental Science & Technology* 34, 4193-4198.
- Won D, Sander DM, Shaw CY, Corsi RL, 2001a. Validation of the surface sink model for sorptive interactions between VOCs and indoor materials. *Atmospheric Environment* 35, 4479-4488.
- Won D, Corsi RL, Rynes M, 2001b. Sorptive interactions between VOCs and indoor materials. *Indoor Air* 11, 246-256.
- Woodfolk JA, Luczynska CM, DeBlay F, Chapman MD, Platts-Mills TAE, 1993. The effect of vacuum cleaners on the concentration and particle-size distribution of airborne cat allergen. *Journal of Allergy and Clinical Immunology* 91, 829-837.

- Wooley J, Nazaroff WW, Hodgson AT, 1990. Release of ethanol to the atmosphere during use of consumer cleaning products. *Journal of the Air & Waste Management Association* 40, 1114-1120.
- Yu J, Flagan RC, Seinfeld JH, 1998. Identification of products containing -COOH , -OH , and -C=O in atmospheric oxidation of hydrocarbons. *Environmental Science & Technology* 32, 2357-2370.
- Zhao P, Siegel JA, Corsi RL, 2005. Experimental characterization of portable ion generators, *Proceedings of Indoor Air 2005*, Beijing, China, pp. 2957-2961.
- Zhu J, Cao XL, Beauchamp R, 2001. Determination of 2-butoxyethanol emissions from selected consumer products and its application in assessment of inhalation exposure associated with cleaning tasks. *Environment International* 26, 589-597.
- Zock JP, Kogevinas M, Sunyer J, Almar E, Muniozguren N, Payo F, Sanchez JL, Anto JM, 2001. Asthma risk, cleaning activities and use of specific cleaning products among Spanish indoor cleaners. *Scandinavian Journal of Work Environment & Health* 27, 76-81.

Publications Produced

Destailats H, Singer BC, Coleman BK, Lunden MM, Hodgson AT, Weschler CJ, and Nazaroff WW, 2005. Secondary pollutants from cleaning products and air fresheners in the presence of ozone, in *Proceedings: Indoor Air 2005, 10th International Conference on Indoor Air Quality and Climate*, X Yang, B Zhao, R Zhao, Eds., Tshinghua University Press, Beijing, China, pp. 2081-2085.

Destailats H, Lunden MM, Singer BC, Coleman BK, Hodgson AT, Weschler CJ, and Nazaroff WW. Indoor secondary pollutants from household product emissions in the presence of ozone. A bench-scale chamber study. Submitted to *Environmental Science & Technology*.

Nazaroff WW, and Weschler CJ, 2004. Cleaning products and air fresheners: Exposure to primary and secondary air pollutants. *Atmospheric Environment* **38**, 2841-2865.

Singer BC, Destailats H, Hodgson AT, Nazaroff WW, 2006. Cleaning products and air fresheners: Emissions and resulting concentrations of glycol ethers and terpenoids. *Indoor Air* (accepted).

Singer BC, Coleman BK, Destailats H, Hodgson AT, Weschler CJ, and Nazaroff CW. Indoor secondary pollutants from cleaning product and air freshener use in the presence of ozone. Submitted to *Atmospheric Environment*.

Glossary of Terms, Abbreviations, and Symbols

2-BE	2-butoxyethanol (C ₆ H ₁₄ O ₂)
2-HE	2-hexyloxyethanol (C ₈ H ₁₈ O ₂)
ach	air changes per hour
ACH	air-exchange rate
ACM	4-acetyl-1-methylcyclohexene
AER	air-exchange rate
AFR	air freshener
AlcOH	saturated alcohol
alkyl	molecular fragment containing only carbon and hydrogen atoms in a chain
amu	atomic mass units
ARB	(California) Air Resources Board
ASTM	American Society for Testing and Materials
Ba	(Tedlar) bag-based screening method
BE	2-butoxyethanol (C ₆ H ₁₄ O ₂)
BFB	1-bromo-4-fluorobenzene
BHT	butylated hydroxytoluene
bk	background
BTC	bathroom & tile cleaner
C	concentration
C	carbon (atom)
CA	California
CARB	California Air Resources Board
CAS	Chemical Abstract Service
C-C	two carbon atoms with a single covalent bond
C=C	two carbon atoms with a double covalent bond
CH ₃ COOH	acetic acid
CH ₃ O ₂	methyl peroxide radical
C _i	mass fraction of compound <i>i</i> in product
CI	confidence interval
Cl ₂	chlorine (gas)
cm	centimeter
Co	continuous
conc.	concentrated
CUC	carpet & upholstery cleaner
d	day
D	daily
Di	direct solvent dilution method
DIS	disinfectant
dM/dlogDp	particle size distribution function, by mass concentration
dN/dlogDp	particle size distribution function, by number concentration
DNPH	dinitrophenylhydrazine
Dp	particle diameter
DST	dusting aid
EBGE	ethylene-based glycol ether
Em	emissions experiment in room-sized test chamber

expt	experiment
$[F]_{produced}$	quantity of formaldehyde generated by reactive chemistry in bench-scale chamber
FEP	fluorinated ethylene propylene
FMP	furniture maintenance product
FPW	floor polish or wax
FS	full strength
ft	foot
FW	formula weight
FWS	floor wax stripper
g	gram
gal	gallon
GC	gas chromatograph
GC/MS	gas chromatography/mass spectrometry
GLC	glass and surface cleaner
glycol ether ^a	a class of chemicals with members that are commonly used as solvents in cleaning products
GM	geometric mean
GMD	geometric mean diameter
GPC	general-purpose cleaner
GPD	general-purpose degreaser
GSD	geometric standard deviation
h	hour
HAP	hazardous air pollutant
HC	hydrocarbon
HCl	hydrochloric acid
He	helium
H ₆ F ₆	hydrogen fluoride (hexamer)
h_i	bimolecular reaction rate for OH with unsaturated species i
h_j	bimolecular reaction rate for OH with saturated species j
H ₂ O	water
HO ₂	hydroperoxy radical
HOCl	hypochlorous acid
HPLC	high performance liquid chromatography
H ₃ PO ₄	phosphoric acid
IARC	International Agency for Research on Cancer
IC	ion chromatography
ID	identification
iF	intake fraction
IPOH	3-isopropenyl-6-oxoheptanal
K	kelvin
k, k_i	second-order rate constant for homogeneous bimolecular reaction
k'	pseudo first-order rate constants
k_a	rate constant for sorptive uptake
k_d	rate constant for desorption
k_{O3}	reaction rate constant for VOC with ozone
k_{OH-TMB}	reaction rate constant for OH-initiated de TMB

kg	kilogram ($= 10^3$ g)
kPa	kilopascal ($= 10^3$ Pa)
L	liter
Lim	<i>d</i> -limonene
m	meter
MBO	2-methyl-3-buten-2-ol
M_{CP}	mass of cleaning product introduced into bag
MeOH	methanol
mg	milligram ($= 10^{-3}$ g)
$M_{i,GC}$	mass of compound <i>i</i> in bag sample as determined from TD-GC/MS analysis
min	minute
mL	milliliter ($= 10^{-3}$ L)
mm	millimeter ($= 10^{-3}$ m)
mM	millimolar ($= 10^{-3}$ molar)
mol	mole
MPS	multipurpose solvent
MRL	minimal risk level
MSD	mass-selective detector
MSDS	material safety data sheet
MTL	metal polish/cleaner
MVT	5-methyl-5-vinyltetrahydrofuran-2-ol
m/z	ion mass-to-charge ratio
<i>n</i>	number of occupants exposed; number of samples collected
na	not available
N ₂	nitrogen (gas)
NaHSO ₄	sodium bisulfate
NaNO ₃	sodium nitrate
NaOCl	sodium hypochlorite
NaOH	sodium hydroxide
nd	not detected
ng	nanogram ($= 10^{-9}$ g)
NHCl ₂	dichloramine
NH ₂ Cl	monochloramine
NH ₃	ammonia
NIST	National Institute of Standards and Technology
NL	not listed
nm	nanometer ($= 10^{-9}$ m)
NO	nitric oxide
[NO]	concentration of nitric oxide
NO ₂	nitrogen dioxide
[NO ₂]	concentration of nitrogen dioxide
NO ₃	nitrate radical
[NO ₃]	ozone concentration
nq	not quantifiable
nr	not recorded
NSRL	no significant risk level

O	occasional
O ₃	ozone
[O ₃]	ozone concentration
[O ₃] _{consumed}	quantity of ozone consumed by reactive chemistry in bench-scale chamber
OCI ⁻	hypochlorite ion
OEHHA	Office of Environmental Health Hazard Assessment
OH	hydroxyl radical
[OH]	concentration of the OH radical
OPC	optical particle counter
OR	odds ratio
OVN	oven cleaner
P	primary constituent (of cleaning product or air freshener)
Pa	pascal, unit of pressure
PCE	perchloroethylene (CCl ₄)
[PCE]	concentration of PCE
PM _{0.1}	particulate matter smaller than 0.1 μm in diameter
PM _{0.4}	particulate matter smaller than 0.4 μm in diameter
PM _{1.1}	particulate matter smaller than 1.1 μm in diameter
PM _{2.5}	particulate matter smaller than 2.5 μm in diameter
PM ₁₀	particulate matter smaller than 10 μm in diameter
P/N	part number
ppb	parts per billion (= 10 ⁻⁹)
ppm	parts per million (= 10 ⁻⁶)
PSL	polystyrene latex
ppt	parts per trillion (= 10 ⁻¹²)
REL	reference exposure level
RfC	reference concentration from chronic inhalation exposure
RH	relative humidity
RO ₂	peroxy radical
ROG	reactive organic gases
RT	retention time
R _{T/P}	ratio of TMB to PCE in chamber air
s	second
S	secondary pollutant
SF ₆	sulfur hexafluoride
sHC	saturated hydrocarbon
[S _j]	concentration of saturated VOC <i>j</i>
SMPS	scanning-mobility particle sizer
SOA	secondary organic aerosol
SRM	spot remover
<i>t</i>	time
T	temperature
TAC	toxic air contaminant
T-AlcOH	terpene alcohol
TD-GC/MS	thermal desorption – gas chromatography/mass spectrometry
Tenax	sorbent used for VOC sampling

terpene	monocyclic hydrocarbons of the formula $C_{10}H_{16}$, obtained from plants
terpenoid	large and diverse class of organic chemicals similar to terpenes
T-HC	terpene hydrocarbon
TIC	total ion current
TMB	trimethylbenzene (C_9H_{12})
[TMB]	concentration of TMB
TO-1	USEPA standard method for measuring VOCs in air
tonne	metric tonne (= 1000 kg)
torr	unit of pressure (= 1/760 of an atmosphere)
TP	trigger pulls
[U_i]	concentration of unsaturated VOC i
U_0	initial concentration of reactive VOC
ultrafine particles	airborne particulate matter with diameter less than 0.1 μm
US	United States
US EPA	United States Environmental Protection Agency
UV	ultraviolet electromagnetic radiation
V_{bag}	total gas volume in sampling bag
VOC	volatile organic compound
V_s	gas sample volume
W	weekly
WDC	wood cleaner
$X_{primary}$	fraction of formaldehyde production owing to primary oxidation
y	year
y_i	formation yield for OH from reaction between ozone and species i
%	percent
λ	air-exchange rate (h^{-1})
τ	characteristic time (e.g., for mixing)
σ	standard deviation
ϕ_F	yield (mole of product per mole of ozone consumed)
$^{\circ}C$	degrees centigrade
μ	(arithmetic) mean
μg	microgram (= 10^{-6} g)
μL	microliter (= 10^{-6} L)
μm	micrometer (= 10^{-6} m)

^a Glycol ethers are characterized in the California Air Resources Board Toxic Air Contaminant Identification Program (<http://www.arb.ca.gov/toxics>) as follows:

“Glycol ethers: includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol ($R(OCH_2CH_2)_n-OR'$), where

$n = 1, 2, \text{ or } 3$

$R = \text{alkyl or aryl groups}$

$R' = R, H, \text{ or groups which, when removed, yield glycol ethers with the structure } R(OCH_2CH_2)_n-OH.$ Polymers are excluded from the glycol category”

For 2-BE, $R = C_4H_9$, $n = 1$, and $R' = H$. For 2-HE, For $R = C_6H_{13}$, $n = 1$, and $R' = H$.